

Cross Sections for Electron Collisions with Nitrogen Molecules

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Cross section data have been compiled for electron collisions with nitrogen molecules, based on 104 references. Cross sections are collected and reviewed for: total scattering, elastic scattering, momentum transfer, excitations of rotational, vibrational, and electronic states, dissociation, ionization, and emission of radiation. For each process, the recommended values of the cross section are presented for use. The literature has been surveyed through the end of 2003. © 2006 American Institute of Physics.

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Key words: cross section; dissociation; elastic scattering; electron collision; emission; excitation; ionization; momentum transfer; N₂; nitrogen; recommended data; total scattering.

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1. Introduction

Nitrogen molecules are the most abundant constituent of the Earth's atmosphere. Electron collisions with nitrogen molecules play a fundamental role, for example, in ionospheric and auroral phenomena in the upper atmosphere of the Earth. They are also important processes in electrical discharges involving atmospheric gases. Those discharges constitute a basic technique in the fields of gaseous electronics and plasma processing.

Almost 20 years ago, the present author and his colleagues published a comprehensive compilation of cross section data on electron collisions with N_2 .¹ (We refer to the paper as I86 hereafter.) Since then, a number of new theoretical and experimental results have been reported on the electron collision with N_2 , due to an improvement or a new development of theoretical and experimental methods. The present paper is the complete update of the previous data compilation (I86) on the $e + \text{N}_2$ collisions.^{2,3}

Because of the importance of the nitrogen molecule, a review of the cross sections for the $e + \text{N}_2$ collisions has been attempted by several authors. Majeed and Strickland⁴ published a set of cross sections for $e + \text{N}_2$ collisions, but mainly for inelastic (i.e., electron energy loss) processes. Zecca *et al.*⁵ and Brunger and Buckman⁶ published a comprehensive data compilation for electron collisions with various molecules, including N_2 . The latter authors concentrated their compilation on the processes of elastic scattering and excitations of discrete states (i.e., nothing being included on ionization and dissociation). The bibliography recently published by Hayashi⁷ is also useful.

Very recently an extensive data compilation has been carried out for electron collisions with a large number of molecules, including nitrogen.⁸ The work reported cross section data on total scattering, elastic scattering, momentum transfer, ionization, electron attachment, and excitation of rotational, vibrational, and electronic states. The present paper is mainly based on this data compilation, but has a wider scope than that. Furthermore significant additional information (e.g., a detailed discussion of emission cross sections and dissociation processes) is given. After reviewing available cross section data, we have determined a set of recommended values of cross section, when possible. The general criteria for the selection of preferred data are as follows:

- (1) In principle, experimental data are preferred to theoretical ones. In some cases, however, elaborate calculations are referred to provide fine details which cannot be experimentally obtained.
- (2) The reliability of the experimental methods employed is critically assessed. Agreement between independent measurements of the same cross section is generally taken as an endorsement of the accuracy of the measured data. A strong emphasis is placed on the consistency of the results taken by different techniques.
- (3) In cases where only a single set of data is available for a given cross section, those data are simply shown here

TABLE 1. Measurements of total scattering cross section for N₂

| Author(s) | Energy range (eV) |
|---|-------------------|
| Blaauw <i>et al.</i> ¹⁰ | 16–700 |
| Kennerly ¹¹ | 0.5–50 |
| Hoffman <i>et al.</i> ¹² | 2.2–700 |
| Garcia <i>et al.</i> ¹³ | 600–5000 |
| Nishimura and Yano ¹⁴ | 7–500 |
| Ferch <i>et al.</i> ¹⁵ | 0.1–1 |
| Nickel <i>et al.</i> ¹⁶ | 4–300 |
| Karwasz <i>et al.</i> ¹⁷ | 250–4000 |
| Xing <i>et al.</i> ¹⁸ | 500–1000 |
| Sun <i>et al.</i> ¹⁹ | 0.08–10 |
| Szmytkowski <i>et al.</i> ²⁰ | 0.4–250 |

(i.e., not designated as recommended), unless there is a strong reason to reject them. Even when multiple sets of data are available, no recommendation is made if there is a significant disagreement among them or they are fragmentary (i.e., only a few data points being reported). In this way, the present paper aims to provide a more complete data set for electron collisions with N₂ than those published before. The literature has been surveyed through the end of 2003.

2. Total Scattering Cross Section

After a careful analysis of the experimental methods for the determination of the total scattering cross section, Q_T , Karwasz *et al.*⁹ have determined the best values of the cross section for a number of molecules. For N₂, they found a good agreement among the cross sections obtained by the measurements listed in Table 1. They took a weighted average of those cross sections to give the best values. The resulting cross sections are shown in Fig. 1 and Table 2, as the recommended values for use. The peak at around 2.3 eV is due to the ²Π_g shape resonance.²¹ The detailed structure of the resonance peak is shown in Fig. 2, according to the measurement by Kennerly¹¹ and Sun *et al.*¹⁹

When compared with the corresponding cross sections reported in I86, the present values of Q_T are in close agreement with them in the energy region above 1 eV. Below 1 eV, the present values are slightly smaller than the previous ones. In the energy range below 1 eV, the Q_T in I86 was based on a preliminary report of Jost *et al.*²² The present Q_T is mainly based on a time of flight (TOF) experiment of Sun *et al.*¹⁹ (and a preliminary report of Ferch *et al.*¹⁵). Recently Hoffmann *et al.*²³ have measured Q_T at the energies below 0.7 eV. They used a very low energy electron beam formed by photoionization of Ar at slightly above the ionization threshold. The Q_T of Hoffmann *et al.* are in agreement with those of Jost *et al.* better than with those of Sun *et al.* In conclusion the present Q_T below 1 eV may have a large uncertainty (up to ±20%).

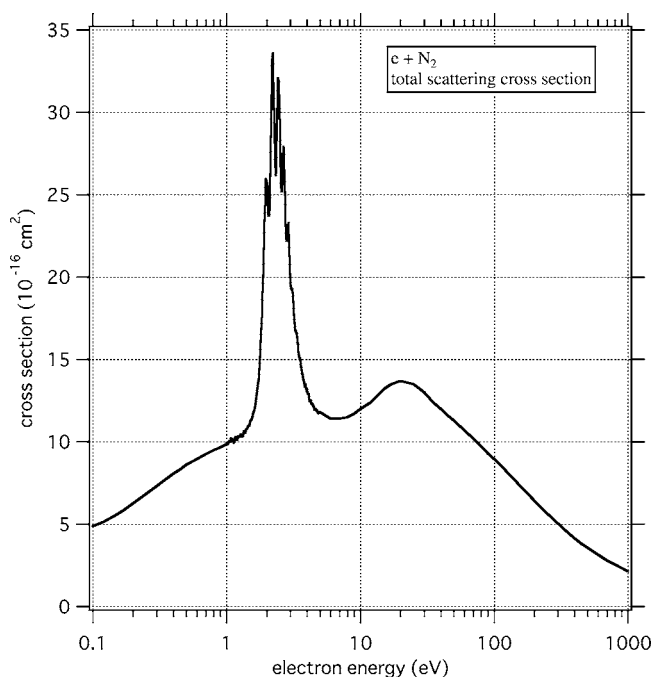


Fig. 1. Recommended values of the total scattering cross section, Q_T , of N₂.

3. Elastic Scattering and Momentum Transfer Cross Sections

Most of the electron beam experiments have insufficient energy resolution to resolve each rotational state of the nitrogen molecule. Hence the elastic cross section obtained experimentally often represents the vibrationally elastic one:

TABLE 2. Recommended total scattering cross section for electron collisions with N₂

| Energy (eV) | Cross section (10 ⁻¹⁶ cm ²) | Energy (eV) | Cross section (10 ⁻¹⁶ cm ²) | Energy (eV) | Cross section (10 ⁻¹⁶ cm ²) |
|------------------|--|------------------|--|-------------|--|
| 0.1 | 4.88 | 3.0 ^a | 21.0 | 70 | 10.2 |
| 0.12 | 5.13 | 3.5 ^a | 14.6 | 80 | 9.72 |
| 0.15 | 5.56 | 4.0 ^a | 13.2 | 90 | 9.30 |
| 0.17 | 5.85 | 4.5 ^a | 12.3 | 100 | 8.94 |
| 0.2 | 6.25 | 5.0 | 11.8 | 120 | 8.33 |
| 0.25 | 6.84 | 6.0 | 11.4 | 150 | 7.48 |
| 0.3 | 7.32 | 7.0 | 11.4 | 170 | 7.02 |
| 0.35 | 7.72 | 8.0 | 11.5 | 200 | 6.43 |
| 0.4 | 8.06 | 9.0 | 11.7 | 250 | 5.66 |
| 0.45 | 8.33 | 10 | 12.0 | 300 | 5.04 |
| 0.5 | 8.61 | 12 | 12.4 | 350 | 4.54 |
| 0.6 | 8.96 | 15 | 13.2 | 400 | 4.15 |
| 0.7 | 9.25 | 17 | 13.5 | 450 | 3.82 |
| 0.8 | 9.48 | 20 | 13.7 | 500 | 3.55 |
| 0.9 | 9.66 | 25 | 13.5 | 600 | 3.14 |
| 1.0 | 9.85 | 30 | 13.0 | 700 | 2.79 |
| 1.2 ^a | 10.2 | 35 | 12.4 | 800 | 2.55 |
| 1.5 ^a | 11.2 | 40 | 12.0 | 900 | 2.32 |
| 1.7 ^a | 13.3 | 45 | 11.6 | 1000 | 2.13 |
| 2.0 ^a | 25.7 | 50 | 11.3 | | |
| 2.5 ^a | 28.5 | 60 | 10.7 | | |

^aOnly representative values are shown in the resonance region. See Fig. 2 for the details of the cross section in this region.

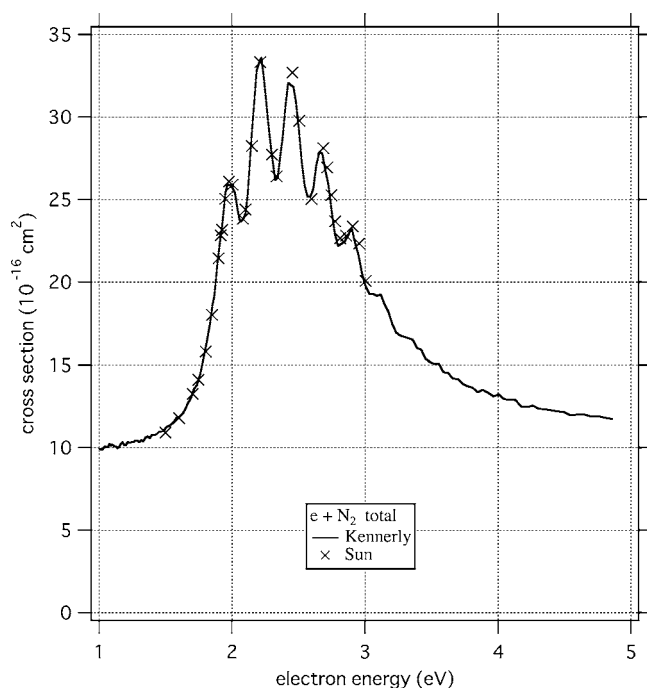


FIG. 2. Total scattering cross section, Q_T , of N_2 in the resonance region, measured by Kennerly¹¹ and by Sun *et al.*¹⁹

i.e., including the cross sections for rotational transition, averaged over the initial rotational states and summed over the final ones. In the present section, therefore, Q_{elas} is defined as the vibrationally elastic cross section. Pure elastic, or rotationally elastic, cross sections are discussed in Section 4.

Using the available data of beam experiments,^{19,24–28} Buckman *et al.*²⁹ have determined the recommended values of Q_{elas} for N_2 at 0.55–100 eV. (For details of the comparison of the measured cross sections, see the review by Brunger and Buckman.⁶) The resulting values are shown in Fig. 3. (In the figure, the recommended cross sections of Buckman *et al.* have been extended to 1000 eV in a way described below.) On the basis of the level of concurrence between the individual measurements considered, Buckman *et al.* estimated the uncertainty to be of the order of $\pm 20\%$. All of the experimental cross sections they used were derived from differential cross section (DCS) measurements. In the resonance region, the cross section is strongly dependent on the incident energy, as well as on the scattering angle. It is, therefore, very difficult for a DCS measurement to determine fine structure of resonance in integrated cross section (ICS).⁶ The cross sections between 1 and 4 eV plotted in Fig. 3 show only a broad envelope of the resonance. When a comparison is made with the Q_{elas} in I86, the two sets of cross sections agree with each other at the energies above 20 eV. In the present paper (i.e., Fig. 3), the Q_{elas} of Buckman *et al.* has been connected with the Q_{elas} in I86 at 100 eV to extend the recommended data up to 1000 eV. The Q_{elas} in I86 in the energy region above 100 eV was based on two sets of beam experiments: Shyn and Carignan²⁵ and DuBois and Rudd.³⁰

Table 3 presents the numerical values of Q_{elas} recommended here.

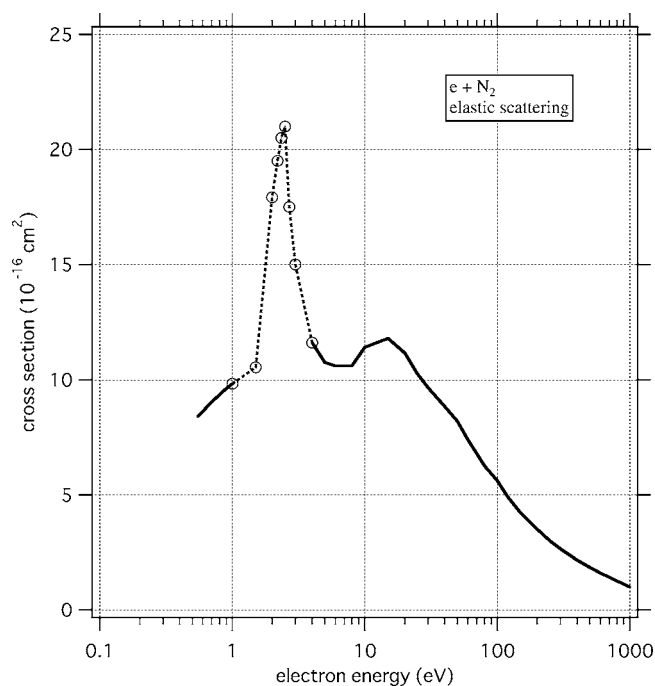


FIG. 3. Recommended values of the elastic scattering cross section, Q_{elas} , of N_2 . In the energy region, 1–4 eV, only an envelope of the resonance cross sections is plotted.

TABLE 3. Recommended elastic scattering cross section for electron collisions with N_2

| Energy (eV) | Cross section (10^{-16} cm^2) | Energy (eV) | Cross section (10^{-16} cm^2) |
|-------------------|---|-------------|---|
| 0.55 | 8.39 | 120 | 4.9 |
| 0.70 | 9.03 | 150 | 4.2 |
| 0.90 | 9.62 | 200 | 3.5 |
| 1.0 | 9.83 | 250 | 3.0 |
| 1.5 ^a | 10.53 | 300 | 2.65 |
| 2.0 ^a | 17.93 | 400 | 2.15 |
| 2.2 ^a | 19.5 | 500 | 1.85 |
| 2.35 ^a | 20.5 | 600 | 1.60 |
| 2.5 ^a | 21.0 | 800 | 1.25 |
| 2.7 ^a | 17.5 | 1000 | 1.00 |
| 3.0 ^a | 15.0 | | |
| 4.0 ^a | 11.6 | | |
| 5.0 | 10.75 | | |
| 6.0 | 10.6 | | |
| 8.0 | 10.6 | | |
| 10 | 11.4 | | |
| 15 | 11.8 | | |
| 20 | 11.15 | | |
| 25 | 10.25 | | |
| 30 | 9.65 | | |
| 40 | 8.85 | | |
| 50 | 8.2 | | |
| 60 | 7.4 | | |
| 80 | 6.25 | | |
| 100 | 5.6 | | |

^aOnly representative values are shown in the resonance region.

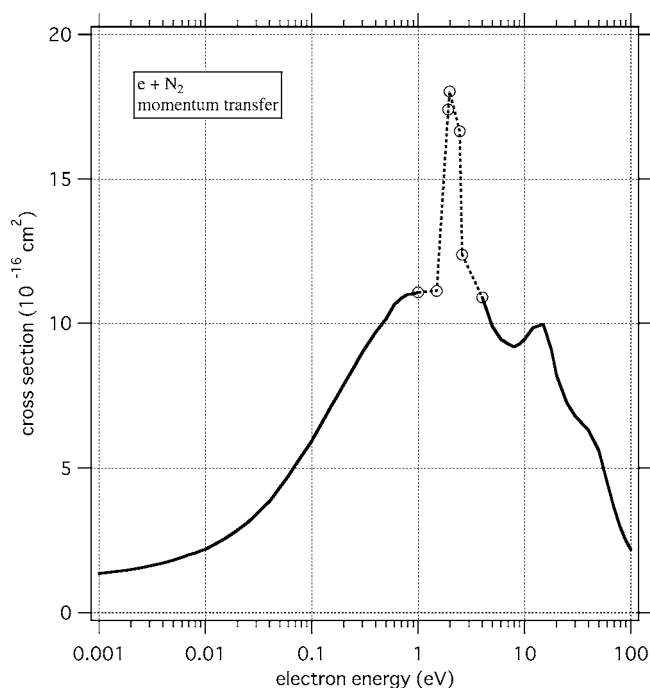


FIG. 4. Recommended values of the momentum transfer cross section, Q_m , of N_2 . In the energy region, 1–4 eV, only an envelope of the resonance cross sections is plotted.

Elford *et al.*³¹ have determined the recommended values of the momentum transfer cross section, Q_m . They based their determination on the swarm experiment by Haddad³² for 0.001–0.5 eV, a theoretical calculation by Sun *et al.*¹⁹ (tabulated in the paper by Robertson *et al.*³³) for 0.5–3.0 eV, and beam measurements of Sun *et al.*¹⁹ and Srivastava *et al.*²⁴ above 4 eV. In the present paper, the cross sections of beam experiment by Sun *et al.*, instead of their theoretical ones, have been chosen in the resonance region (0.5–3.5 eV). The resulting cross sections are shown in Fig. 4 and Table 4. In the figure, the cross sections in the resonance region show only a broad envelope of the resonance similarly to the case of elastic cross sections (Fig. 3). As was estimated by Elford *et al.* the uncertainty of the present values of Q_m are within $\pm 5\%$ for 0.001–0.5 eV and $\pm 20\%$ for 3.5–100 eV. No uncertainty limit can be given for the resonance region.

In the energy region below 0.5 eV, the present Q_m completely agrees with the previous one in I86. In the energy region above 0.5 eV, the two sets of Q_m differ to some extent.

4. Rotational Excitation

Brunger *et al.*³⁴ have determined the recommended values of the cross section for the rotational excitation Q_{rot} for $J=0 \rightarrow 2$, where J is the rotational quantum number of the molecule. They are shown in Fig. 5 and Table 5. The rotational constant B_0 of N_2 in the ground vibrational state is 2.4668×10^{-4} eV, which gives the excitation energy for the $J=0 \rightarrow 2$ transition to be 1.48×10^{-3} eV. Brunger *et al.*³⁴

TABLE 4. Recommended momentum transfer cross section for electron collisions with N_2

| Energy (eV) | Cross section (10^{-16} cm ²) | Energy (eV) | Cross section (10^{-16} cm ²) | Energy (eV) | Cross section (10^{-16} cm ²) |
|-------------|--|--------------------|--|-------------|--|
| 0.001 | 1.357 | 0.07 | 5.10 | 4 | 10.90 |
| 0.0015 | 1.426 | 0.08 | 5.41 | 5 | 9.90 |
| 0.0018 | 1.464 | 0.09 | 5.69 | 6 | 9.45 |
| 0.002 | 1.490 | 0.1 | 5.95 | 7 | 9.29 |
| 0.0025 | 1.550 | 0.12 | 6.45 | 8 | 9.19 |
| 0.003 | 1.620 | 0.15 | 7.10 | 9 | 9.29 |
| 0.004 | 1.718 | 0.18 | 7.59 | 10 | 9.45 |
| 0.005 | 1.810 | 0.2 | 7.90 | 12 | 9.84 |
| 0.006 | 1.908 | 0.25 | 8.50 | 15 | 9.97 |
| 0.007 | 2.000 | 0.3 | 9.00 | 18 | 9.07 |
| 0.008 | 2.062 | 0.4 | 9.70 | 20 | 8.20 |
| 0.009 | 2.131 | 0.5 | 10.16 | 25 | 7.25 |
| 0.01 | 2.190 | 0.6 | 10.65 | 30 | 6.80 |
| 0.012 | 2.342 | 0.7 | 10.87 | 40 | 6.31 |
| 0.015 | 2.550 | 0.8 | 11.00 | 50 | 5.60 |
| 0.018 | 2.729 | 0.9 | 11.03 | 60 | 4.51 |
| 0.02 | 2.850 | 1 | 11.07 | 70 | 3.59 |
| 0.025 | 3.12 | 1.5 ^a | 11.12 | 80 | 2.94 |
| 0.03 | 3.40 | 1.92 ^a | 17.40 | 90 | 2.50 |
| 0.04 | 3.85 | 1.98 ^a | 18.03 | 100 | 2.19 |
| 0.05 | 4.33 | 2.46 ^a | 16.65 | | |
| 0.06 | 4.72 | 2.605 ^a | 12.38 | | |

^aOnly representative values are shown in the resonance region.

based their values on the theoretical cross sections obtained by Morrison *et al.*³⁵ They estimated the uncertainty of the cross sections to be $\pm 10\%$. The validity of the present cross section has been confirmed with a swarm experiment up to

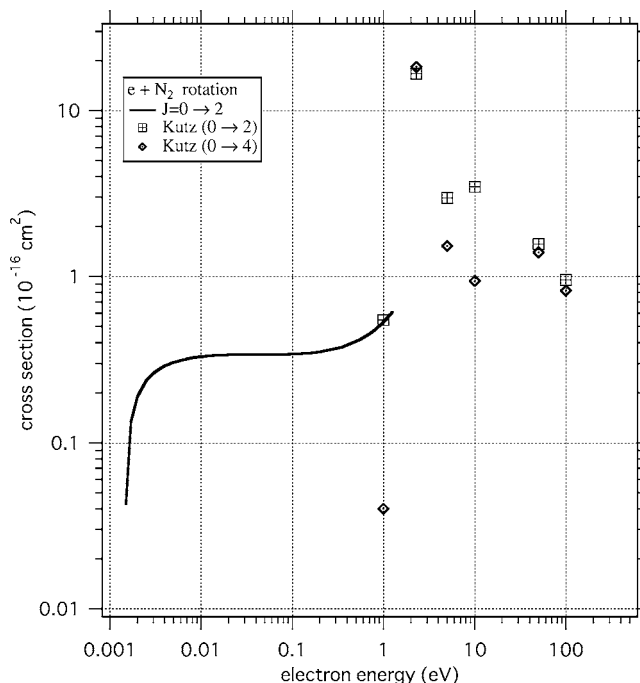


FIG. 5. Cross sections for the rotational transitions in N_2 . Solid line shows the recommended values for the transition $J=0 \rightarrow 2$. Above 1 eV, representative values of the cross section calculated by Kutz and Meyer³⁹ for the transitions $J=0 \rightarrow 2, 4$ are plotted.

TABLE 5. Recommended cross section for the rotational transition $J=0 \rightarrow 2$ for electron collisions with N_2

| Energy (eV) | Cross section (10^{-16} cm^2) | Energy (eV) | Cross section (10^{-16} cm^2) |
|----------------|--|----------------|--|
| 0.0015 | 0.043 | 0.020 | 0.337 |
| 0.0017 | 0.134 | 0.030 | 0.338 |
| 0.0020 | 0.190 | 0.040 | 0.338 |
| 0.0025 | 0.236 | 0.060 | 0.338 |
| 0.0030 | 0.262 | 0.080 | 0.339 |
| 0.0035 | 0.278 | 0.100 | 0.340 |
| 0.0040 | 0.290 | 0.120 | 0.342 |
| 0.0045 | 0.298 | 0.140 | 0.344 |
| 0.0050 | 0.305 | 0.160 | 0.346 |
| 0.0055 | 0.309 | 0.200 | 0.351 |
| 0.0060 | 0.313 | 0.350 | 0.375 |
| 0.0070 | 0.319 | 0.550 | 0.415 |
| 0.0080 | 0.324 | 0.700 | 0.450 |
| 0.0090 | 0.327 | 0.800 | 0.475 |
| 0.010 | 0.329 | 1.000 | 0.529 |
| 0.015 | 0.335 | 1.250 | 0.608 |

0.2 eV.³³ At the same time, the theoretical result of Onda,³⁶ which was cited in I86, was found to be inconsistent with the swarm experiment.³³ Very recently Telega *et al.*³⁷ reported their theoretical cross section for the rotational excitations $J=0 \rightarrow 2,4$ of N_2 at the collision energies from the respective thresholds to 1.5 eV. They employed the rotationally close-coupling method to produce a correct behavior of the cross section near threshold. The result of Telega *et al.* well reproduced the experimental cross section in the vicinity of the threshold (say, <0.01 eV). However, their values increase too rapidly with increasing energy, compared with the cross sections shown in Fig. 5. This is probably due to the insufficient accuracy of the potential model adopted for the electron exchange and target polarization.

For the rotational excitation at the energies above 1 eV, two sets of new data are available: DCS measurement by Gote and Ehrhardt³⁸ and a theoretical calculation by Kutz and Meyer.³⁹ Gote and Ehrhardt measured DCS for the rotational excitations $J=0 \rightarrow 0,2,4,6,8$ at the scattering angles $10^\circ - 160^\circ$ for the energy region 10–200 eV, but they derived no ICS from them. Kutz and Meyer calculated Q_{rot} over a wide range of energy (0.01–1000 eV). They obtained cross sections for the rotational transitions, $J=0 \rightarrow 0,2,4,6$. Figure 5 shows the representative values of their cross sections. To test the accuracy of the result of Kutz and Meyer, their cross sections summed over the final rotational states, $\sum_J Q_{\text{rot}}(0 \rightarrow J)$, is compared with the experimental value of Q_{elas} (in Fig. 3). The theoretical values are 10.8, 63.0, 12.3, 5.83 in units of 10^{-16} cm^2 at 1, 2.3 (resonance peak), 10, 100 eV, respectively. The corresponding experimental values are 9.83, 21.0, 11.4, 5.6. From this we can conclude that:

- (1) at the resonance peak, the theoretical cross section is too large, and
- (2) otherwise, the theoretical values are consistent with the experiment.

We expect, therefore, that Fig. 5 shows typical values of Q_{rot}

in the energy range above 1 eV, except in the vicinity of resonance peak. This conclusion is consistent with the result of the previous studies cited in I86. In the resonance region (1.5–3.0 eV), I86 shows the theoretical cross sections of Onda.³⁶ The peak value of his cross section in the resonance region ($3.15 \times 10^{-16} \text{ cm}^2$ for $J=0 \rightarrow 2$ and $6.73 \times 10^{-16} \text{ cm}^2$ for $J=0 \rightarrow 4$) is much less than the corresponding value in Fig. 5. At the energies above 5 eV, I86 cites two theoretical calculations (Onda³⁶ and Rumble *et al.*⁴⁰). Both of the calculations give the values in good agreement with those in Fig. 5. For example, at 10 eV, Onda, Rumble *et al.*, and Kutz and Meyer give, respectively, $Q_{\text{rot}}(0 \rightarrow 2) = 3.86, 3.84, 3.47 \times 10^{-16} \text{ cm}^2$ and $Q_{\text{rot}}(0 \rightarrow 4) = 1.35, 0.99, 0.94 \times 10^{-16} \text{ cm}^2$, and at 50 eV they are $Q_{\text{rot}}(0 \rightarrow 2) = 1.63, 1.64, 1.57 \times 10^{-16} \text{ cm}^2$ and $Q_{\text{rot}}(0 \rightarrow 4) = 1.36, 1.41, 1.40 \times 10^{-16} \text{ cm}^2$. The experimental evidence, however, is only fragmentary. From the deconvolution of the elastic peak in the electron energy loss spectra, Jung *et al.*⁴¹ derived the rotational cross section at the resonance peak (2.47 eV). Since they employed the high- J approximation to derive the cross section, their result cannot be directly compared with the present data. Furthermore I86 reported a preliminary result of the beam experiment at 5–20 eV by Tanaka, which are consistent with the theoretical values shown above. In any case, more definite experimental data are needed to confirm the above conclusion.

Theoretical calculations can provide rotationally elastic (i.e., $J=0 \rightarrow 0$) cross sections. Kutz and Mayer,³⁹ for example, showed that the rotationally elastic cross section dominates over the rotationally inelastic ones at the energies above 1 eV. In other words, the difference in the magnitudes of Q_{elas} in Fig. 3 and $Q_{\text{rot}}(J=0 \rightarrow 2)$ in Fig. 5 comes mainly from the rotationally elastic process. The DCS measurement of Gote and Ehrhardt³⁸ indicates, however, that the relative magnitudes of the elastic and inelastic cross sections sensitively depend on the scattering angle. No measurement of ICS has been reported on the rotationally elastic cross section, except for one data point obtained by Jung *et al.*⁴¹

5. Vibrational Excitation

For the excitation of vibrational state, $v=0 \rightarrow 1$ (v being the vibrational quantum number), we adopt the cross sections recommended by Brunger *et al.*³⁴ The excitation energy of the process $v=0 \rightarrow 1$ is 0.289 eV. They have used all available results of beam experiments: Sohn *et al.*²⁶ for the energies <1 eV, Brennan *et al.*²⁷ and Sun *et al.*¹⁹ for 1.5–5 eV, and Tanaka *et al.*⁴² for 7.5–30 eV. The resulting Q_{vib} (shown in Fig. 6 and Table 6) agrees almost completely with the corresponding values in I86. The uncertainty of the recommended cross section was estimated to be $\pm 30\%$ for the energies less than 1 eV, $\pm 25\%$ for 1.5–5 eV, and $\pm 26\%$ for 7.5–30 eV. As in the case of elastic cross sections, the present Q_{vib} in Fig. 6 shows only a broad envelope of the resonance in the 1–5 eV region.

The $^2\Pi_g$ shape resonance in the vibrational excitation of N_2 has been extensively studied theoretically and experimen-

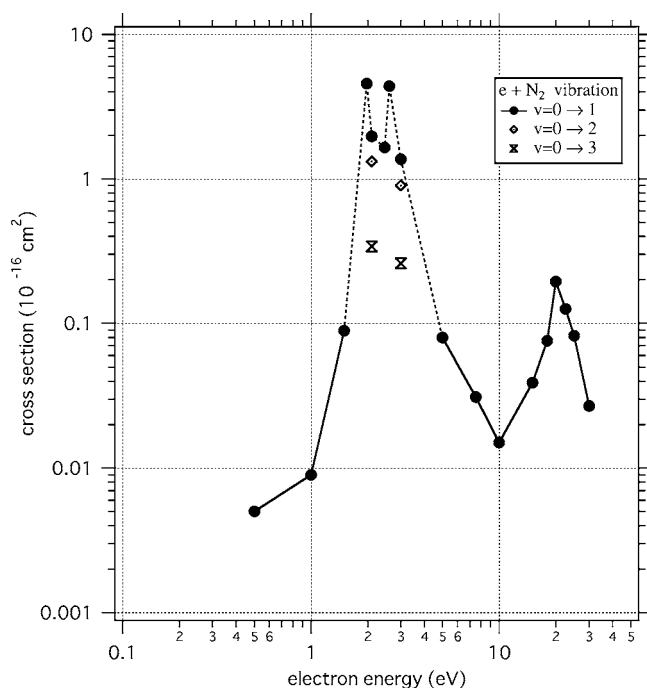


FIG. 6. Recommended values of the cross section for the vibrational excitation $v=0 \rightarrow 1$. In the energy region, 1.5–5 eV, only an envelope of the resonance cross sections is plotted. Typical values for the excitation of higher states ($v=0 \rightarrow 2,3$) are also shown in the resonance region.

tally (see, for recent works, Sun *et al.*,¹⁹ Grimm-Bosbach *et al.*,⁴³ Vicic *et al.*,⁴⁴ and Sweeney and Shyn⁴⁵). It is, however, very difficult to obtain accurate values of Q_{vib} in the resonance region. The theoretical values of the resonant cross section depend sensitively on the theoretical model adopted. It is almost impossible for a beam experiment to derive the fine structure of the resonance in ICS. Further-

TABLE 6. Recommended cross section for the vibrational excitation $v=0 \rightarrow 1$ for electron collisions with N_2

| Energy (eV) | Cross section (10^{-16} cm^2) |
|--------------------|---|
| 0.5 | 0.005 |
| 1.0 | 0.009 |
| 1.5 ^a | 0.089 |
| 1.98 ^a | 4.560 |
| 2.1 ^a | 1.970 |
| 2.46 ^a | 1.650 |
| 2.605 ^a | 4.400 |
| 3.0 ^a | 1.370 |
| 5.0 | 0.080 |
| 7.5 | 0.031 |
| 10 | 0.015 |
| 15 | 0.039 |
| 18 | 0.076 |
| 20 | 0.195 |
| 22.5 | 0.126 |
| 25 | 0.082 |
| 30 | 0.027 |

^aOnly representative values are shown in the resonance region. See Fig. 7 for the details of the vibrational cross sections in this region.

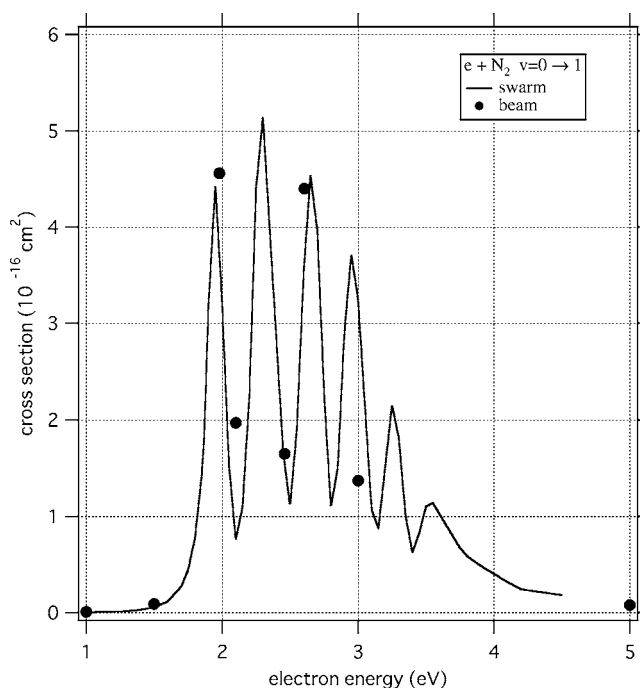


FIG. 7. Vibrational cross sections for $v=0 \rightarrow 1$ in the resonance region. The results obtained from a swarm analysis⁴⁶ are compared with the recommended values based on a beam measurement (shown in Fig. 6).

more, since the resonant cross section strongly depends on the incident energy, a discrepancy between theory and experiment may be easily arisen from a small error in the energy calibration in experiments. Very recently, Campbell *et al.*⁴⁶ have determined the best values of the vibrational cross section in the resonance region. Their values are based mainly on the cross section derived in a swarm experiment by Ohmori *et al.*⁴⁷ That is, they were determined so as to reproduce the measured transport parameters. Campbell *et al.* slightly modified the original values of Ohmori *et al.*, with a more careful analysis of the swarm measurement. The vibrational cross section for the transition $v=0 \rightarrow 1$ recommended by Campbell *et al.* is shown in Fig. 7. They are consistent with the best cross sections shown in Fig. 6.

In the resonance region, high harmonics of the vibration are excited upon electron collisions. Typical values for the transitions $v=0 \rightarrow 2,3$ are plotted in Fig. 6, according to the compilation of Brunger *et al.*³⁴ The relative magnitudes of the cross section for the excitations up to $v=17$ have been reported by Allan,⁴⁸ Huo *et al.*,⁴⁹ and Vicic *et al.*⁴⁴

6. Excitation of Electronic States

Table 7 shows the list of cross sections presented here for the excitation of electronic states of N_2 and N_2^+ with the respective values of excitation energy. A more comprehensive table of energy levels and spectroscopic constants of the excited states is given in I86. In the following, the cross sections are discussed separately for the lower states (i.e., located below 12.5 eV) and the higher ones (above 12.5 eV).

TABLE 7. List of the cross sections for the excitation of electronic states of N_2 and N_2^+ ^a

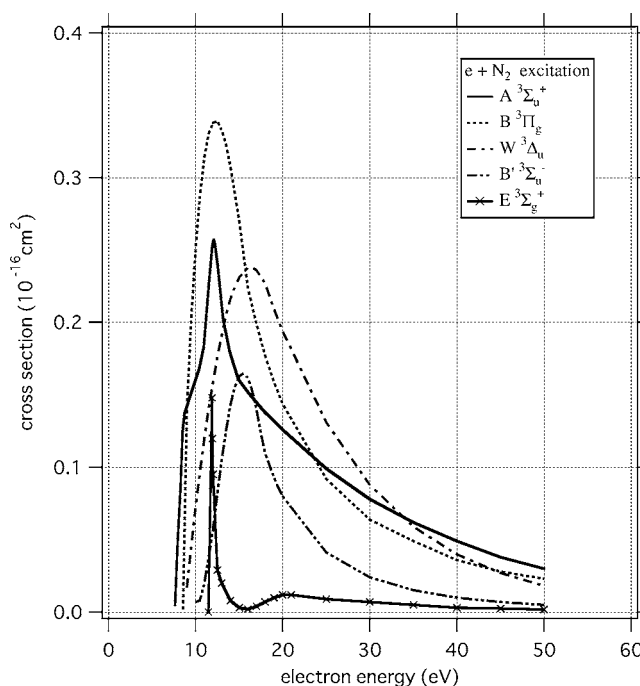
| State | T_0 (eV) ^{b,c} | Figure | Table |
|--------------------|---------------------------|--------|-------|
| N_2 | | | |
| $A^3\Sigma_u^+$ | 6.169 | 8 | 8 |
| $B^3\Pi_g$ | 7.353 | 8 | 8 |
| $W^3\Delta_u$ | 7.362 | 8 | 8 |
| $B'^3\Sigma_u^-$ | 8.165 | 8 | 8 |
| $a'^1\Sigma_u^-$ | 8.399 | 9 | 9 |
| $a^1\Pi_g$ | 8.549 | 10 | 9 |
| $w^1\Delta_u$ | 8.890 | 9 | 9 |
| $C^3\Pi_u$ | 11.032 | 11 | 10 |
| $E^3\Sigma_g^+$ | 11.875 ^d | 8 | 10 |
| $a''^1\Sigma_g^+$ | 12.255 | 9 | 10 |
| $b^1\Pi_u$ | 12.500 | 12 | |
| $c_4'^1\Sigma_u^+$ | 12.935 | 13 | |
| $b'^1\Sigma_u^+$ | 12.854 | 14 | |
| N_2^+ | | | |
| $X^2\Sigma_g^+$ | 15.581 | 25 | 18 |
| $A^2\Pi_u$ | 16.699 | | 18 |
| $B^2\Sigma_u^+$ | 18.751 | | 18 |

^aMore detailed lists of the energy states are given in I86.^bEnergy of the lowest vibrational state relative to $X^1\Sigma_g^+(v=0)$.^cSummarized in I86.^dUncertain.

6.1. Lower States

In 1977, the JPL group^{50,51} published their result of extensive measurements of excitation cross section, Q_{exc} , of electronic states of N_2 . They used an electron energy loss measurement to obtain the cross sections. Later Trajmar *et al.*⁵² renormalized those cross sections with the use of improved data on elastic cross section. The previous review (I86) adopted those renormalized values as recommended ones. Later a similar electron energy loss measurement was done by an Australian group. They reported their measured DCS in 1990.⁵³ By using a molecular phase shift analysis technique, they extrapolated their DCS towards the forward and the backward scattering directions where they could not measure cross sections. Then they derived ICS and reported them in 2001.⁵⁴ A swarm experiment also provides cross section data for excitations of electronic states. Ohmori *et al.*,⁴⁷ for example, made an extensive analysis of swarm data to determine cross sections for N_2 . In some cases, there is a significant discrepancy among the values of measured cross sections for N_2 . To resolve such a discrepancy, an elaborate *ab initio* calculation is useful. Gillan *et al.*⁵⁵ reported their calculation based on the *R*-matrix theory for several excited states. Since the *R*-matrix method is expected to be most reliable in low energy region, they obtained ICS at the energies below 18 eV.

Recently Brunger *et al.*³⁴ have determined the best values of Q_{exc} for N_2 on the basis of the works described above: i.e., the two sets of beam measurements (Trajmar *et al.*⁵² and Campbell *et al.*⁵⁴), a swarm experiment (Ohmori *et al.*⁴⁷), and a comprehensive theory (Gillan *et al.*⁵⁵). In some cases (see below), those data have been supplemented with a few other available sets of experimental cross sections. When the

FIG. 8. Recommended values of the cross sections for the excitation of electronic states of N_2 : $A^3\Sigma_u^+$, $B^3\Pi_g$, $W^3\Delta_u$, $B'^3\Sigma_u^-$, and $E^3\Sigma_g^+$.

R-matrix method calculation is available (i.e., for the $A^3\Sigma_u^+$, $B^3\Pi_g$, $W^3\Delta_u$, $B'^3\Sigma_u^-$ states), the theoretical cross sections have been referred to for the detailed structure near threshold. Otherwise a weighted average of the experimental cross sections has been taken with a polynomial least square fit to the energy dependence of the individual set of the cross sections. Thus the estimated uncertainty indicates the degree of the concurrence of the individual experimental results. In the following, the conclusion of Brunger *et al.* is adopted to give recommended values. For detailed comparisons of the available data, see the original papers (e.g., Campbell *et al.*) and a recent review of Brunger and Buckman.⁶

(1) $A^3\Sigma_u^+$, $B^3\Pi_g$, $W^3\Delta_u$, $B'^3\Sigma_u^-$, $a'^1\Sigma_u^-$, $w^1\Delta_u$, $a''^1\Sigma_g^+$. Figures 8 and 9 (and Tables 8, 9, and 10) show the recommended values of Q_{exc} for these states. Brunger *et al.*³⁴ estimated the uncertainty of the recommended values as $\pm 35\%$ ($\pm 40\%$ at the energies below 15 eV) for $A^3\Sigma_u^+$, $\pm 35\%$ for $B^3\Pi_g$ and $W^3\Delta_u$, $\pm 40\%$ for $B'^3\Sigma_u^-$, $\pm 30\%$ for $a'^1\Sigma_u^-$ and $w^1\Delta_u$, and $\pm 33\%$ for $a''^1\Sigma_g^+$ states.

(2) $a^1\Pi_g$. Besides the two sets of beam measurement mentioned above,^{52,54} another two beam experiments have been reported for the excitation of $a^1\Pi_g$ state. Finn and Doering⁵⁶ made an electron energy loss measurement, but normalized their data using an emission cross section of the Lyman–Birge–Hopfield (LBH) system (see below). Mason and Newell⁵⁷ directly detected the excited molecule in $a^1\Pi_g$ state. Brunger *et al.*³⁴ took consideration of these two works also. Their recommended values of Q_{exc} for $a^1\Pi_g$ state are shown in Fig. 10. They claimed $\pm 25\%$ uncertainty of their result.

As is discussed in Section 7, Q_{exc} for $a^1\Pi_g$ state can be derived from the emission cross section for the LBH system.

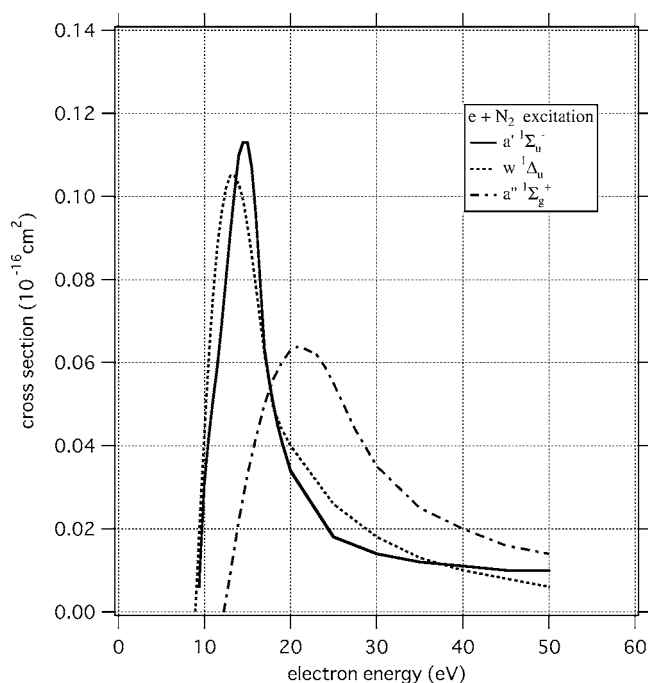


FIG. 9. Recommended values of the cross section for the excitation of electronic states of N_2 : $a' \ ^1\Sigma_u^-$, $w \ ^1\Delta_u$, and $a'' \ ^1\Sigma_g^+$.

Figure 10 also shows the Q_{exc} thus derived from the Q_{emis} obtained by Ajello and Shemansky⁵⁸ (see Sec. 7). The two sets of the cross sections shown in Fig. 10 are in reasonable agreement, except in the peak region. Considering rather large uncertainties claimed (i.e., $\pm 25\%$ for the data of Brunger *et al.*³⁴ and $\pm 22\%$ for the data derived by Ajello and Shemansky), however, the two sets of cross sections in Fig. 10 are consistent with each other even in the peak region.

Table 9 gives the recommended values of Q_{exc} for $a \ ^1\Pi_g$ state.

(3) $C \ ^3\Pi_u$. Zubek and King⁵⁹ and Poparic *et al.*⁶⁰ employed a beam experiment to determine Q_{exc} for the excitation of $C \ ^3\Pi_u$ state. Considering these two works, together with those mentioned above, Brunger *et al.*³⁴ have determined their recommended values of Q_{exc} for the C state. The result is shown in Fig. 11. An uncertainty of $\pm 30\%$ was estimated in this case by Brunger *et al.*

The emission of the second positive system can provide Q_{exc} for the C state (see Sec. 7). Figure 11 also shows the Q_{exc} thus derived from Q_{emis} measured by Shemansky *et al.*⁶¹ (with uncertainty of $\pm 13.5\%$). The agreement of the two sets of cross section in Fig. 11 is fairly good.

Table 10 gives the recommended values of Q_{exc} for $C \ ^3\Pi_u$ state.

TABLE 8. Recommended cross sections for the electron impact excitation of the electronic states of N_2 (Part 1)

| $A \ ^3\Sigma_u^+$ | | $B \ ^3\Pi_g$ | | $W \ ^3\Delta_u$ | | $B' \ ^3\Sigma_u^-$ | |
|--------------------|---|---------------|---|------------------|---|---------------------|---|
| Energy (eV) | Cross section (10^{-16} cm^2) | Energy (eV) | Cross section (10^{-16} cm^2) | Energy (eV) | Cross section (10^{-16} cm^2) | Energy (eV) | Cross section (10^{-16} cm^2) |
| 7.65 | 0.005 | 8.55 | 0.002 | 9 | 0.017 | 10 | 0.007 |
| 7.96 | 0.048 | 9.0 | 0.141 | 9.5 | 0.045 | 10.5 | 0.008 |
| 8.26 | 0.085 | 9.5 | 0.202 | 10 | 0.072 | 11 | 0.019 |
| 8.52 | 0.125 | 10 | 0.250 | 10.5 | 0.096 | 11.5 | 0.037 |
| 8.74 | 0.137 | 10.5 | 0.287 | 11 | 0.119 | 12 | 0.058 |
| 9.57 | 0.153 | 11 | 0.313 | 11.5 | 0.140 | 12.5 | 0.082 |
| 10.40 | 0.168 | 11.5 | 0.330 | 12 | 0.159 | 13 | 0.105 |
| 10.96 | 0.183 | 12 | 0.338 | 12.5 | 0.176 | 13.5 | 0.125 |
| 11.53 | 0.226 | 12.5 | 0.339 | 13 | 0.191 | 14 | 0.143 |
| 11.88 | 0.251 | 13 | 0.333 | 13.5 | 0.205 | 14.5 | 0.155 |
| 11.97 | 0.254 | 13.5 | 0.323 | 14 | 0.216 | 15 | 0.163 |
| 12.10 | 0.257 | 14 | 0.308 | 14.5 | 0.224 | 15.5 | 0.165 |
| 12.23 | 0.254 | 14.5 | 0.290 | 15 | 0.231 | 16 | 0.162 |
| 12.54 | 0.239 | 15 | 0.270 | 16 | 0.238 | 16.5 | 0.153 |
| 13.15 | 0.202 | 16 | 0.224 | 16.5 | 0.238 | 17 | 0.140 |
| 13.90 | 0.180 | 17 | 0.199 | 17 | 0.236 | 17.5 | 0.124 |
| 14.85 | 0.162 | 18 | 0.177 | 18 | 0.227 | 18 | 0.110 |
| 15 | 0.160 | 19 | 0.159 | 19 | 0.209 | 18.5 | 0.101 |
| 16 | 0.152 | 20 | 0.144 | 20 | 0.194 | 19 | 0.093 |
| 17 | 0.145 | 25 | 0.092 | 25 | 0.131 | 19.5 | 0.086 |
| 18 | 0.138 | 30 | 0.064 | 30 | 0.088 | 20 | 0.080 |
| 19 | 0.132 | 35 | 0.049 | 35 | 0.059 | 25 | 0.041 |
| 20 | 0.126 | 40 | 0.036 | 40 | 0.040 | 30 | 0.024 |
| 25 | 0.099 | 45 | 0.028 | 45 | 0.027 | 35 | 0.015 |
| 30 | 0.078 | 50 | 0.023 | 50 | 0.018 | 40 | 0.010 |
| 35 | 0.062 | | | | | 45 | 0.007 |
| 40 | 0.049 | | | | | 50 | 0.005 |
| 45 | 0.038 | | | | | | |
| 50 | 0.030 | | | | | | |

TABLE 9. Recommended cross sections for the electron impact excitation of the electronic states of N₂ (Part 2)

| $a' \ ^1\Sigma_u^-$ | | $a \ ^1\Pi_g$ | | $w \ ^1\Delta_u$ | |
|---------------------|---|---------------|---|------------------|---|
| Energy (eV) | Cross section (10^{-16} cm^2) | Energy (eV) | Cross section (10^{-16} cm^2) | Energy (eV) | Cross section (10^{-16} cm^2) |
| 9.4 | 0.006 | 8 | 0.001 | 8.9 | 0.0001 |
| 9.5 | 0.011 | 8.5 | 0.016 | 9.0 | 0.002 |
| 10 | 0.031 | 9 | 0.038 | 9.5 | 0.024 |
| 10.5 | 0.042 | 9.5 | 0.066 | 10 | 0.043 |
| 11 | 0.051 | 10 | 0.099 | 10.5 | 0.061 |
| 11.5 | 0.059 | 11 | 0.174 | 11 | 0.076 |
| 12 | 0.069 | 12 | 0.254 | 11.5 | 0.088 |
| 12.5 | 0.080 | 13 | 0.329 | 12 | 0.096 |
| 13 | 0.091 | 14 | 0.394 | 12.5 | 0.102 |
| 13.5 | 0.101 | 15 | 0.443 | 13 | 0.105 |
| 14 | 0.110 | 15.5 | 0.459 | 13.5 | 0.105 |
| 14.5 | 0.113 | 16 | 0.469 | 14 | 0.103 |
| 15 | 0.113 | 16.5 | 0.473 | 14.5 | 0.099 |
| 15.5 | 0.107 | 17 | 0.471 | 15 | 0.093 |
| 16 | 0.095 | 17.5 | 0.462 | 15.5 | 0.086 |
| 16.5 | 0.079 | 18 | 0.446 | 16 | 0.078 |
| 17 | 0.063 | 19 | 0.394 | 17 | 0.062 |
| 17.5 | 0.056 | 21.5 | 0.300 | 18 | 0.049 |
| 18 | 0.050 | 25 | 0.258 | 19 | 0.044 |
| 18.5 | 0.045 | 30 | 0.215 | 20 | 0.040 |
| 19 | 0.041 | 35 | 0.185 | 25 | 0.026 |
| 20 | 0.034 | 40 | 0.161 | 30 | 0.018 |
| 25 | 0.018 | 45 | 0.144 | 35 | 0.013 |
| 30 | 0.014 | 50 | 0.129 | 40 | 0.010 |
| 35 | 0.012 | 60 | 0.108 | 45 | 0.008 |
| 40 | 0.011 | 70 | 0.092 | 50 | 0.006 |
| 45 | 0.010 | 80 | 0.081 | | |
| 50 | 0.010 | 90 | 0.072 | | |
| | | 100 | 0.065 | | |

TABLE 10. Recommended cross sections for the electron impact excitation of the electronic states of N₂ (Part 3)

| $C \ ^3\Pi_u$ | | $E \ ^3\Sigma_g^+$ | | $a'' \ ^1\Sigma_g^+$ | |
|---------------|---|--------------------|---|----------------------|---|
| Energy (eV) | Cross section (10^{-16} cm^2) | Energy (eV) | Cross section (10^{-16} cm^2) | Energy (eV) | Cross section (10^{-16} cm^2) |
| 11 | 0.001 | 11.5 | 0.000 | 12.25 | 0.000 |
| 11.5 | 0.074 | 11.9 | 0.148 | 13 | 0.009 |
| 12 | 0.147 | 11.95 | 0.120 | 14 | 0.022 |
| 12.5 | 0.229 | 12.0 | 0.095 | 15 | 0.033 |
| 13 | 0.335 | 12.5 | 0.029 | 16 | 0.042 |
| 13.5 | 0.455 | 13 | 0.020 | 17 | 0.050 |
| 14 | 0.551 | 14 | 0.008 | 18 | 0.056 |
| 14.5 | 0.583 | 15 | 0.003 | 19 | 0.060 |
| 15 | 0.551 | 16 | 0.002 | 20 | 0.063 |
| 15.7 | 0.478 | 17 | 0.004 | 21 | 0.064 |
| 16 | 0.447 | 18 | 0.007 | 22 | 0.063 |
| 16.5 | 0.403 | 19 | 0.010 | 23 | 0.062 |
| 17 | 0.353 | 20 | 0.012 | 24 | 0.059 |
| 17.5 | 0.302 | 21 | 0.012 | 25 | 0.055 |
| 18 | 0.276 | 25 | 0.009 | 27.5 | 0.044 |
| 18.5 | 0.258 | 30 | 0.007 | 30 | 0.035 |
| 19 | 0.242 | 35 | 0.005 | 35 | 0.025 |
| 19.5 | 0.226 | 40 | 0.003 | 40 | 0.020 |
| 20 | 0.212 | 45 | 0.0025 | 45 | 0.016 |
| 25 | 0.122 | 50 | 0.0018 | 50 | 0.014 |
| 30 | 0.077 | | | | |
| 35 | 0.052 | | | | |
| 40 | 0.038 | | | | |
| 45 | 0.028 | | | | |
| 50 | 0.022 | | | | |

(4) $E \ ^3\Sigma_g^+$. The excitation cross section of $E \ ^3\Sigma_g^+$ state has a sharp peak in the vicinity of the threshold. This has been identified with a core-excited shape resonance.⁶² Two groups have determined the resonant cross section with the use of direct detection of the molecule in the metastable E state.^{63,64} The magnitudes of the two sets of cross section differ significantly from one another. By using a trochoidal electron spectrometer, Poparich *et al.*^{65,66} determined the absolute values of the cross section at 11.94 and 12.14 eV. This measurement supported one set of the cross section⁶³ against the other.⁶⁴ Brunger *et al.*³⁴ have determined their recommended values of the Q_{exc} for the E state, considering five sets of beam measurements.^{52,54,59,60,63} The resulting cross section is included in Fig. 8 and Table 10. The $\pm 40\%$ uncertainty was claimed for the result.

6.2. Higher States

Chutjian *et al.*⁶⁷ measured cross sections for the transitions in the 12.5–14.2 eV energy-loss region. They reported their ICS at two points of incident energy: 40 and 60 eV. Trajmar *et al.*⁵² renormalized them later. Those renormalized

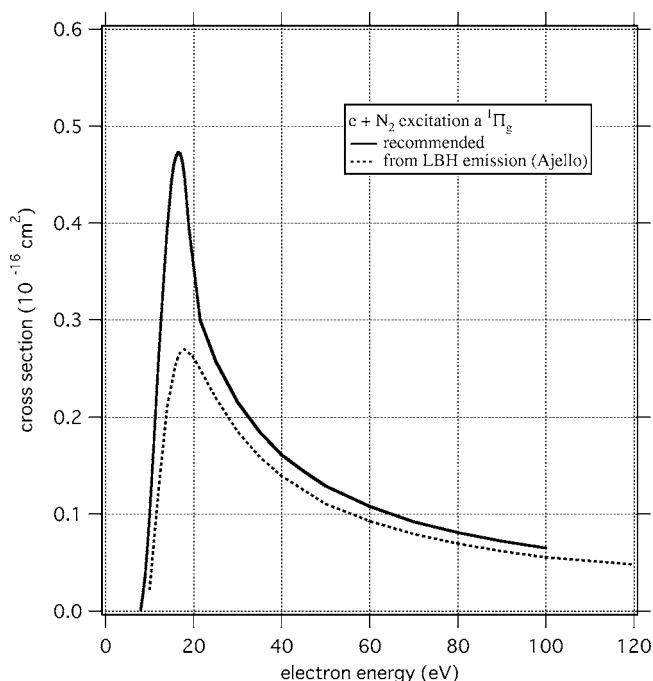


FIG. 10. Cross sections for the excitation of $a \ ^1\Pi_g$ state of N₂. The recommended values are compared with those derived from the emission cross section for the LBH system by Ajello and Shemansky.⁵⁸

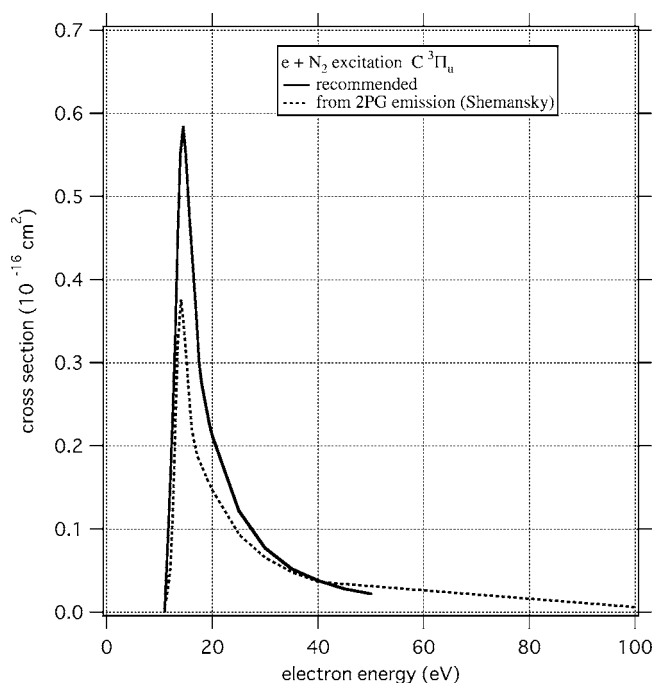


FIG. 11. Cross sections for the excitation of $C^3\Pi_u$ state of N_2 . The recommended values are compared with those derived from the emission cross section for the 2nd positive system by Shemansky *et al.*⁶¹

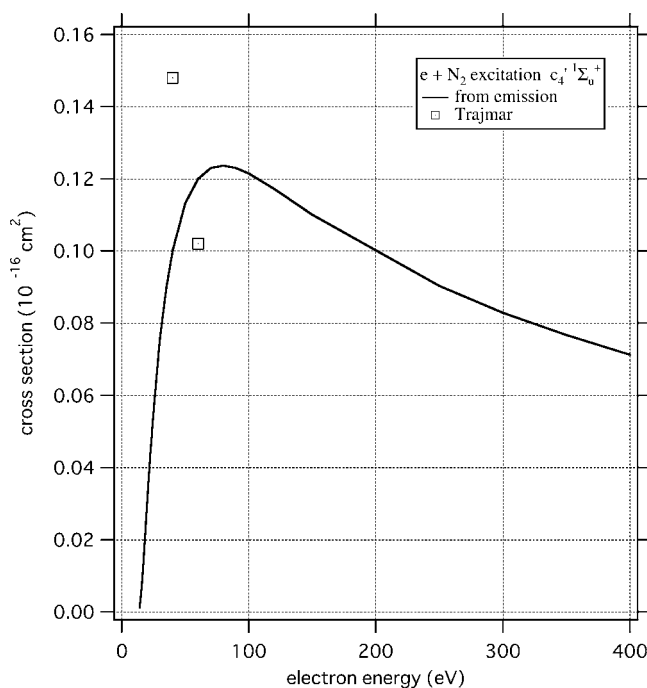


FIG. 13. Excitation cross section for the $c_4'^1\Sigma_u^+$ state of N_2 . The cross sections determined with an electron energy loss measurement by Trajmar *et al.*⁵² are compared with those derived from an emission measurement.⁷⁰

values were cited in I86. For the following three excited states, Q_{exc} can be derived also from Q_{emis} . No new information is available for other four (i.e., $F^3\Pi_u$, $G^3\Pi_u$, $c^1\Pi_u$, and $o^1\Pi_u$) states.

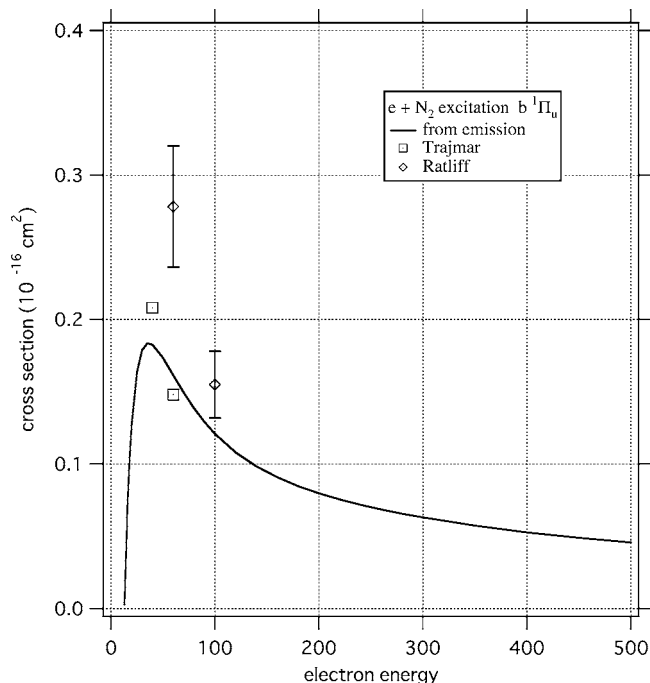


FIG. 12. Excitation cross section for the $b^1\Pi_u$ state of N_2 . The cross sections determined with an electron energy loss measurement by Trajmar *et al.*⁵² and by Ratliff *et al.*⁶⁹ are compared with those derived from an emission measurement.⁶⁸

(1) $b^1\Pi_u$. From the Q_{emis} for the Birge–Hopfield system, Q_{exc} for the $b^1\Pi_u$ state can be determined. Figure 12 shows the Q_{exc} thus derived from the Q_{emis} obtained by James *et al.*⁶⁸ (see Sec. 7), in comparison with the Q_{exc} reported by Trajmar *et al.*⁵² There is a good agreement between the two sets of cross sections. For the $b^1\Pi_u$ state, another measurement of DCS was reported. Ratliff *et al.*⁶⁹ made an electron energy loss measurement for N_2 at 60 and 100 eV to obtain Q_{exc} for the b state. Those cross sections are also plotted in Fig. 12. At 60 eV, the value of Ratliff *et al.* is a factor 2 larger than the one of Trajmar *et al.* Ratliff *et al.* claimed that this discrepancy is ascribed to the inadequate subtraction of background contribution for the elastic cross section in the experiment of Trajmar's group. From Fig. 12, however, the value of Trajmar *et al.* at 60 eV is found closer to the Q_{exc} derived from emission measurement than that of Ratliff *et al.* At 100 eV, the Q_{exc} of Ratliff *et al.* becomes close to the value derived from emission measurement.

From a comparison of Q_{exc} and Q_{emis} , James *et al.*⁶⁸ concluded that, once excited, 95% of the $b^1\Pi_u$ state predissociates.

(2) $c_4'^1\Sigma_u^+$. From the Q_{emis} for the Carroll–Yoshino system, the Q_{exc} for the c_4' state can be derived (see Sec. 7). Figure 13 shows the Q_{exc} thus determined from the emission cross section obtained by Ajello *et al.*,⁷⁰ in comparison with the values of Trajmar *et al.*⁵² There is a large disagreement between the two sets of cross sections at 40 eV, while at 60 eV they become closer to each other.

(3) $b'^1\Sigma_u^+$. From the Q_{emis} for the Birge–Hopfield II system, the Q_{exc} for the $b'^1\Sigma_u^+$ state can be obtained (see Sec.

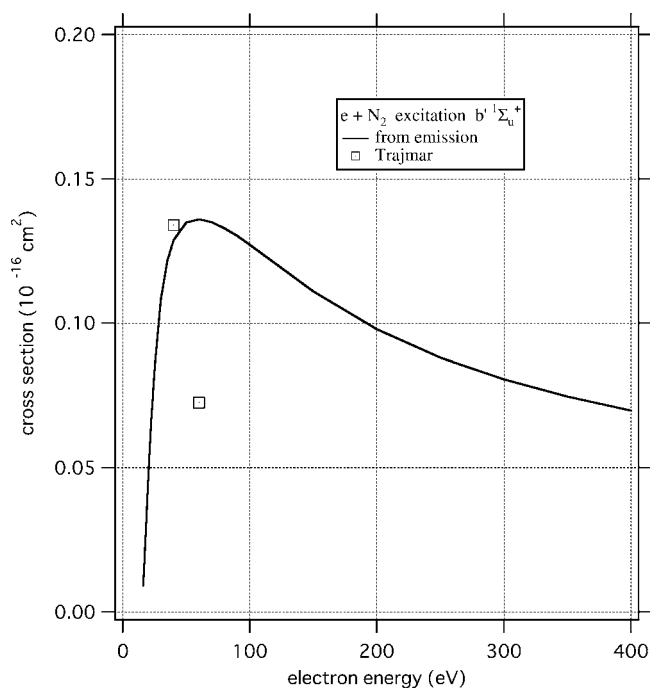


FIG. 14. Excitation cross section for the $b' \, ^1\Sigma_u^+$ state of N_2 . The cross sections determined with an electron energy loss measurement by Trajmar *et al.*⁵² are compared with those derived from the emission measurement.⁷⁰

7). Figure 14 compares the Q_{exc} determined from the emission measurement by Ajello *et al.*⁷⁰ with the values of Trajmar *et al.*⁵² In this case, the two sets of cross sections agree with each other at 40 eV, but disagree considerably at 60 eV. Ajello *et al.* concluded that 84% of the $b' \, ^1\Sigma_u^+$ state predissociates after being excited.

In conclusion, it is difficult to recommend any cross section for the excitation of the states with the threshold above 12.5 eV. Figures 12, 13, and 14, however, give a rough idea about the magnitude and the energy dependence of the Q_{exc} for the $b \, ^1\Pi_u$, $c'_4 \, ^1\Sigma_u^+$, and $b' \, ^1\Sigma_u^+$ states, respectively. The transitions from the ground state ($X \, ^1\Sigma_g^+$) to these excited states are dipole allowed. Hence, the excitation cross sections for these states are expected to have a sizable magnitude even at a high energy of collision. This is indicated by the Q_{exc} derived from emission measurements.

7. Emission Cross Sections

When an electron collides with a nitrogen molecule, radiations in a wide range of wavelengths are emitted. In the following, emissions from excited states of neutral molecules (N_2^*) and from the dissociative fragments (N^* and N^{+*}) are summarized separately. Emission from the excited state of molecular ion (N_2^{+*}) will be discussed in Sec. 9.

7.1. Emission from N_2^*

Figure 15 shows the cross sections for the typical emissions from N_2^* . The numerical values of the Q_{emis} for the three strongest lines are given in Table 11.

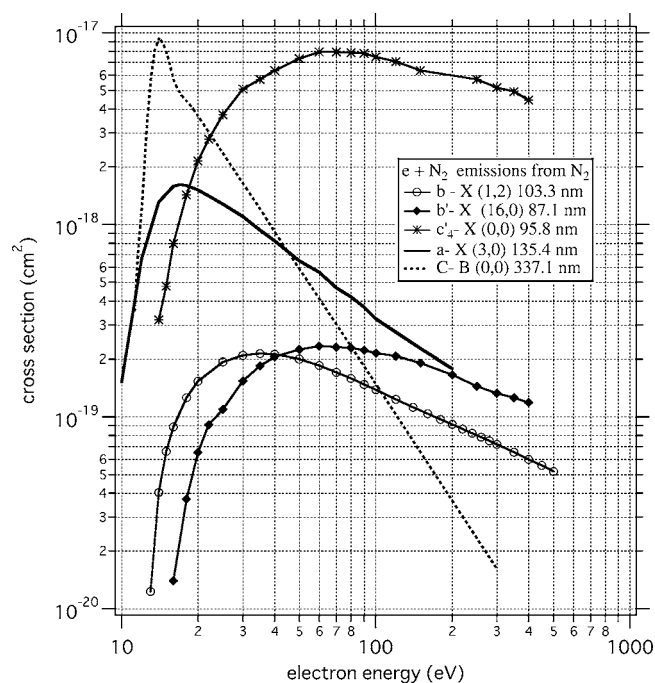


FIG. 15. Emission cross sections for the (0,0) band (at 337.1 nm) of the second positive system,⁶¹ the (3,0) band (at 135.4 nm) of the LBH system,⁵⁸ the (1,2) band (at 103.3 nm) of the BH system,⁶⁸ the (0,0) band (at 95.8 nm) of the Carroll–Yoshino system,⁷⁰ and the (16,0) band (at 87.1 nm) of the BH II system.⁷⁰ The cross sections for the 337.1 nm and the 135.4 nm have been renormalized as is described in text.

TABLE 11. Emission cross sections for electron collisions with N_2

| $a-X$ at 135.4 nm | | $C-B$ at 337.1 nm | | c'_4-X at 95.8 nm | |
|-------------------|---|-------------------|---|---------------------|---|
| Energy (eV) | Cross section (10^{-18} cm^2) | Energy (eV) | Cross section (10^{-18} cm^2) | Energy (eV) | Cross section (10^{-18} cm^2) |
| 10 | 0.152 | 11.23 | 0.352 | 14 | 0.3 |
| 12 | 0.662 | 11.64 | 0.761 | 15 | 0.5 |
| 14 | 1.308 | 12.05 | 1.32 | 16 | 0.79 |
| 16 | 1.583 | 12.46 | 2.72 | 18 | 1.4 |
| 17 | 1.615 | 12.67 | 3.72 | 20 | 2.1 |
| 18 | 1.599 | 13.08 | 5.98 | 22 | 2.8 |
| 20 | 1.518 | 13.49 | 8.13 | 25 | 3.7 |
| 25 | 1.276 | 14.10 | 9.44 | 30 | 5.1 |
| 30 | 1.098 | 14.72 | 8.45 | 35 | 5.7 |
| 35 | 0.937 | 15.13 | 7.63 | 40 | 6.4 |
| 40 | 0.824 | 15.54 | 6.72 | 50 | 7.3 |
| 50 | 0.646 | 16.15 | 5.49 | 60 | 7.95 |
| 60 | 0.565 | 17.18 | 4.72 | 70 | 7.95 |
| 70 | 0.468 | 18.20 | 4.35 | 80 | 7.9 |
| 80 | 0.420 | 19.02 | 4.04 | 90 | 7.8 |
| 90 | 0.372 | 20.05 | 3.67 | 100 | 7.5 |
| 100 | 0.323 | 25.17 | 2.33 | 120 | 7.1 |
| 150 | 0.226 | 30.09 | 1.63 | 150 | 6.4 |
| 200 | 0.178 | 35.01 | 1.21 | 250 | 5.7 |
| | | 40.14 | 0.910 | 300 | 5.2 |
| | | 100 | 0.148 | 350 | 4.9 |
| | | 150 | 0.0655 | 400 | 4.5 |
| | | 200 | 0.0366 | | |
| | | 300 | 0.0162 | | |

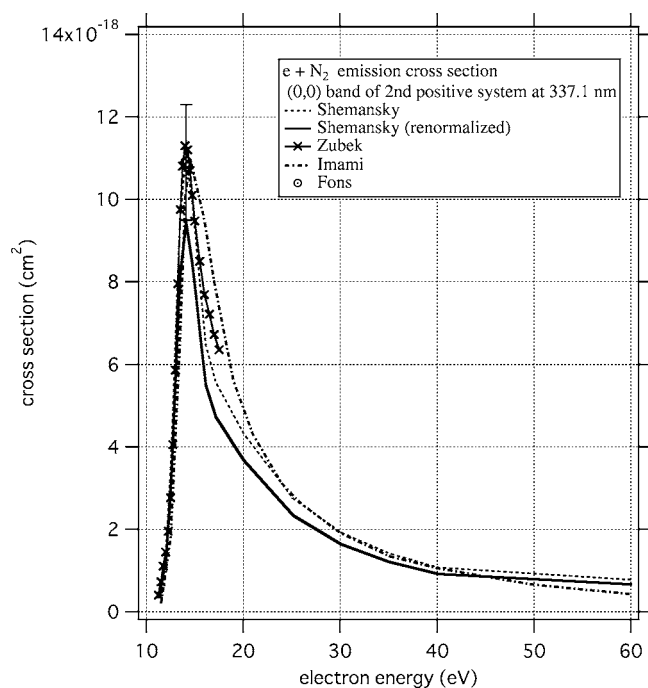


FIG. 16. Emission cross sections for the (0,0) band (at 337.1 nm) of the second positive system. Four different measurements are compared: Zubek,⁷¹ Fons *et al.*,⁷⁵ Imami and Borst,⁷⁴ and Shemansky *et al.*⁶¹ (with and without renormalization).

(1) Second positive system $C^3\Pi_u \rightarrow B^3\Pi_g$. Since the publication of I86, three groups^{61,71,75} reported a measurement of the emission of this system. Zubek⁷¹ measured the (0,0) band at 337 nm over the electron energies from threshold to 17.5 eV. He normalized his measurement to the averaged value of the maximum cross sections of previous measurements (i.e., $11.28 \times 10^{-18} \text{ cm}^2$ at 14.1 eV). Shemansky *et al.*⁶¹ measured the (0,0) (at 337 nm) and (1,0) (at 316 nm) bands for the electron energies 11.23–40.4 eV. They fitted their Q_{emis} with an analytical formula to extrapolate their measured values to higher energies (up to 300 eV). As a normalization, Shemansky *et al.* used the Q_{emis} for the 1st negative system emission (i.e., the $B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$ transition) from N_2^+ . They adopted the value of the cross section obtained by Borst and Zipf.⁷² As is stated in Sec. 9, Doering and Yang⁷³ measured the cross section for the production of the $B^2\Sigma_u^+$ state of N_2^+ with use of the ($e, 2e$) method. From that they determined the best value of the Q_{emis} for the 391.4 nm line of the first negative system to be $14.8 \times 10^{-18} \text{ cm}^2$ at 100 eV. Following this, the Q_{emis} of Borst and Zipf should be reduced by 14.9% and hence the Q_{emis} for the second positive system obtained by Shemansky *et al.* should be reduced by the same amount.

Figure 16 compared the Q_{emis} for the (0,0) band obtained by Zubek⁷¹ with the corresponding values of Shemansky *et al.*⁶¹ with and without renormalization of the latter. The figure also shows one of the older measurements cited in I86, i.e., that of Imami and Borst.⁷⁴ The results of the three measurements are consistent with each other, though the renormalized value of Shemansky *et al.* (which is tabulated in

Table 11 and reproduced in Fig. 15) is a little too small. Shemansky *et al.* claimed $\pm 13.5\%$ uncertainty for their Q_{emis} .

Fons *et al.*⁷⁵ measured Q_{emis} for the second positive system at the electron energies up to 600 eV. They reported the excitation function in a relative scale and an absolute value of the maximum cross section. Their peak value for the (0,0) band ($10.9 \pm 1.4 \times 10^{-18} \text{ cm}^2$) is consistent with the original (i.e., before renormalization) value of Shemansky *et al.*⁶¹ They found that the Q_{emis} decays in proportion to $E^{-2.3}$ with increasing energy. This is slightly different from the trend (i.e., E^{-2}) estimated by Shemansky *et al.*⁶¹

If we can assume no cascade contribution to the emission, we can relate the emission cross section for the (v', v'') band, $Q_{v', v''}$, to the excitation cross section, Q_{exc} , of the upper state of the respective band in the following manner:

$$Q_{v'} = \sum_{v''} Q_{v', v''}, \quad (1)$$

$$Q_{\text{exc}} = \sum_{v'} Q_{v'}. \quad (2)$$

Theoretically we have relations

$$Q_{v', v''} = \frac{A_{v', v''}}{A_{v'}} Q_{v'}, \quad (3)$$

$$Q_{v'} = q_{v'} Q_{\text{exc}}. \quad (4)$$

Here $A_{v', v''}$ and $A_{v'}$ are the band and total transition probabilities and $q_{v'}$ is the Franck–Condon factor from the ground vibrational state. Shemansky *et al.*⁶¹ found from their measurement at 20 eV

$$\frac{Q_{00}}{Q_{v'=0}} = 0.475, \quad (5)$$

$$\frac{Q_{v'=0}}{\sum_{v'} Q_{v'}} = 0.529. \quad (6)$$

Then they obtained the relation at 20 eV

$$\frac{Q_{00}}{Q_{\text{exc}}} = 0.251. \quad (7)$$

This was almost in agreement with the ratio (0.266) estimated from the transition probability and the Franck–Condon factor. Now the Q_{exc} for the C state is estimated from the Q_{00} measured by Shemansky *et al.*⁶¹ (and renormalized as stated above), assuming the above ratio [Eq. (7)] for all the electron energies considered. The resulting Q_{exc} is shown in Fig. 11 in comparison with the values obtained from the electron energy loss measurement.

(2) LBH system $a^1\Pi_g \rightarrow X^1\Sigma_g^+$. Ajello and Shemansky⁵⁸ measured Q_{emis} for the (3,0) band at 135.4 nm at the electron energies from threshold (16 eV) to 200 eV. They normalized their result to the cross section of the Lyman α emission from H_2 . They used the value ($8.18 \times 10^{-18} \text{ cm}^2$ at 100 eV) measured by Shemansky *et al.*⁷⁶ In a review of the vacuum ultraviolet (VUV) measurements of electron-impact emission

from atoms and molecules, Van der Burgt *et al.*⁷⁷ determined the best value of the cross section for the Lyman α emission from H_2 to be $7.3 \times 10^{-18} \text{ cm}^2$ at 100 eV. Accordingly the cross section of Ajello and Shemansky should be multiplied by $7.3/8.18 = 0.892$. The Q_{emis} for the 135.4 nm line thus renormalized is shown in Fig. 15 and Table 11.

In a manner similar to the case of the second positive system, Ajello and Shemansky⁵⁸ derived Q_{exc} for the $a^1\Pi_g$ state from the Q_{emis} they measured. The resulting Q_{exc} should be renormalized in the same way as for their Q_{emis} (i.e., as stated above). The renormalized values of Q_{exc} are plotted in Fig. 10 and compared with the recommended cross sections based on the direct measurement.

In I86, the Q_{emis} measured by Ajello⁷⁸ was cited for the LBH system. According to Ajello and Shemansky,⁵⁸ those values were found too large for the collision energies above 30 eV, due to a problem of backscattering of secondary electrons from the Faraday cup.

(3) Birge–Hopfield system $b^1\Pi_u \rightarrow X^1\Sigma_g^+$. James *et al.*⁶⁸ measured the Q_{emis} for the (1,2) band at 103.3 nm over the energy range from threshold to 400 eV. As for the normalization, they used the most recent Q_{emis} of the Lyman α radiation from H_2 (i.e., the same value as recommended by van der Burgt *et al.*⁷⁷). The Q_{emis} measured by James *et al.* is shown in Fig. 15. They claimed $\pm 22\%$ error for their result. According to James *et al.*, the Q_{emis} obtained by Zipf and Gorman,⁷⁹ which was cited in I86, is too high probably because of the blend of other emissions.

On the basis of an analytical model of modified Born approximation, James *et al.* derived Q_{exc} for the $b^1\Pi_u$ state from their Q_{emis} for the Birge–Hopfield system. The resulting values of Q_{exc} are shown in Fig. 12.

(4) Carroll–Yoshino system $c'_4{}^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ and Birge–Hopfield II system $b'{}^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$. Ajello *et al.*⁷⁰ measured the (0,0) band of the Carroll–Yoshino system at 95.8 nm and the (16,0) band of the Birge–Hopfield II system at 87.1 nm over the energy range from threshold to 400 eV. They adopted the most recent values of Q_{emis} for the Lyman α emission from H_2 for the normalization. Their Q_{emis} (with uncertainty of $\pm 22\%$) for both the bands are shown in Fig. 15. The emission cross sections for the 95.8 nm are tabulated in Table 11. According to Ajello *et al.*, the old data cited in I86 for the Carroll–Yoshino system are not adequate because of insufficient caution taken in the measurement. Assuming no cascade contribution, Ajello *et al.* derived the Q_{exc} for the $c'_4{}^1\Sigma_u^+$ and $b'{}^1\Sigma_u^+$ states from their Q_{emis} . The results are shown in Figs. 13 and 14.

(5) Other emissions. Filippelli *et al.*⁸⁰ measured the Q_{emis} for the fourth positive system $D^3\Sigma_u^+ \rightarrow B^3\Pi_g$. They showed the energy dependence of the Q_{emis} for the (0,1) band at 234.6 nm for the energies from threshold to 400 eV. The maximum value is $3.57 \times 10^{-20} \text{ cm}^2$ at 14.1 eV. The total emission cross section from the D ($v=0$) state was found to be $1.3 \times 10^{-19} \text{ cm}^2$ at the maximum. Thus the cascade contribution of the $D \rightarrow B$ emission to the $B \rightarrow A$ one is very small.

Filippelli *et al.*⁸⁰ also measured the Q_{emis} for the Gaydon–

TABLE 12. Measurements of emission from dissociation fragments of N_2 , reported since 1985^a

| Author(s) | Wavelength range (nm) | Dissociation fragment(s) |
|------------------------------------|-----------------------|--------------------------|
| Forand <i>et al.</i> ⁸⁸ | 90–130 | N* |
| Ajello and Shemansky ⁵⁸ | 116–174 | N* |
| Smirnov ⁸² | 380–940 | N* |
| Rall <i>et al.</i> ⁸³ | 380–700 | N* |
| Rall <i>et al.</i> ⁸⁴ | 380–700 | N ⁺ * |
| Ajello <i>et al.</i> ⁷⁰ | 45–102 | N*, N ⁺ * |
| James <i>et al.</i> ⁶⁸ | 102–134 | N*, N ⁺ * |

^aFor the measurements before 1984, see the review I86.

Herman singlet system $c'_4{}^1\Sigma_u^+ \rightarrow a^1\Pi_g$. They showed the relative energy dependence of the Q_{emis} for the (0,0) band (at 282.7 nm) and (0,4) band (at 346.3 nm) over the energy range from threshold to 200 eV. The Q_{emis} for the (0,0) band, for example, has the maximum value of $1.30 \times 10^{-20} \text{ cm}^2$ at 78.5 eV. From their study, they concluded that c'_4 state almost exclusively decays to the ground (X) state (i.e., the $c'_4 \rightarrow a$ branching ratio is very small).

Allen *et al.*⁸¹ measured the Q_{emis} for

$$y^1\Pi_g \rightarrow w^1\Delta_u$$

$$y^1\Pi_g \rightarrow a'{}^1\Sigma_u^-$$

$$x^1\Sigma_g^+ \rightarrow a'{}^1\Sigma_u^-$$

$$o_3^1\Pi_u \rightarrow a^1\Pi_g$$

transitions. They measured the energy dependence of the Q_{emis} for some specific bands of these transitions in relative scale, with its maximum values in absolute scale. The emissions are in the wavelength range 200–310 nm. The maximum values of the Q_{emis} are typically less than or on the order of 10^{-20} cm^2 .

7.2. Emission from N* and N⁺*

Since the completion of the previous review (I86), several groups reported their measurements of the emission from the dissociation fragments. Those are listed in Table 12. In the following, several prominent lines are discussed in detail. The Q_{emis} for those lines measured by Aarts and de Heer⁸⁵ are shown in Table 13 as a representative. For other lines, the original papers listed in Table 12 should be referred to.

(1) $N\ 2p^4\ ^4P - 2p^3\ ^4S^\circ$ at 113.4 nm. The Q_{emis} obtained by Aarts and de Heer⁸⁵ and by Stone and Zipf⁸⁶ are compared in Fig. 17 with each other. According to van der Burgt *et al.*⁷⁷ the values of Stone and Zipf should be renormalized by multiplying by $7.3/12 = 0.608$. Figure 17 shows the renormalized values of Stone and Zipf. The cross sections of Aarts and de Heer and those of Stone and Zipf have a similar energy dependence, but different absolute magnitudes. Considering rather large uncertainties ($\pm 30\%$ for Aarts and de Heer and $\pm 25\%$ for Stone and Zipf), these two results are consistent with each other. James *et al.*⁶⁸ also measured the line but only at 100 eV. As is seen in Fig. 17, their cross section is in close agreement with the (renormalized) Q_{emis} of Stone and Zipf.

(2) $N\ 3s\ ^4P - 2p^3\ ^4S^\circ$ at 120.0 nm. Five sets of Q_{emis} are available for this line.^{58,68,85,87,88} Figure 18 shows all of

TABLE 13. Cross sections for the emission from dissociation fragments (N and N⁺), measured by Aarts and de Heer⁸⁵

| Energy (eV) | 113.4 nm (N) (10 ⁻¹⁸ cm ²) | 120.0 nm (N) (10 ⁻¹⁸ cm ²) | 124.3 nm (N) (10 ⁻¹⁸ cm ²) | 149.4 nm (N) (10 ⁻¹⁸ cm ²) | 108.4 nm (N ⁺) (10 ⁻¹⁸ cm ²) |
|----------------|--|--|--|--|--|
| 50 | | 5.06 | 1.79 | 2.00 | 2.28 |
| 60 | 1.05 | 5.06 | 1.66 | 2.00 | 2.51 |
| 80 | 1.13 | 4.86 | 1.60 | 1.95 | 2.81 |
| 100 | 1.05 | 4.72 | 1.52 | 1.88 | 3.00 |
| 150 | 0.92 | 4.07 | 1.23 | 1.72 | 2.83 |
| 200 | 0.78 | 3.47 | 1.01 | 1.43 | 2.42 |
| 300 | 0.62 | 2.78 | 0.73 | 1.12 | 1.92 |
| 400 | 0.47 | 2.20 | 0.59 | 0.88 | 1.46 |
| 500 | 0.39 | 1.91 | 0.50 | 0.76 | 1.27 |
| 600 | | 1.66 | 0.40 | 0.63 | 1.08 |
| 800 | 0.24 | 1.42 | 0.34 | 0.51 | 0.87 |
| 1000 | 0.22 | 1.22 | 0.26 | 0.42 | 0.72 |

them. Following the recommendation of van der Burgt *et al.*,⁷⁷ the cross sections of Mumma and Zipf,⁸⁷ Ajello and Shemansky,⁵⁸ and Forand *et al.*⁸⁸ have been renormalized. James *et al.*⁶⁸ and Forand *et al.*⁸⁸ reported their cross section at 100 and 200 eV, respectively. The four sets of data (i.e., Mumma and Zipf, Ajello and Shemansky, Forand *et al.*, and James *et al.*) are in good agreement with each other. The values of Aarts and de Heer⁸⁵ are larger than those four but not inconsistent with them, if we consider the large uncertainty ($\pm 30\%$) of the former. The data of Ajello⁷⁸ (which was cited in I86) are now known to be incorrect (see, for example, Ajello and Shemansky⁵⁸).

(3) $N\ 3s'\ ^2D-2p\ ^3D^\circ$ at 124.3 nm and $3s\ ^2P-2p\ ^3D^\circ$ at 149.4 nm. Three sets of Q_{emis} ^{58,85,87} available for these emissions are compared in Figs. 19 and 20. Here the values of Mumma and Zipf,⁸⁷ and Ajello and Shemansky,⁵⁸ have been renormalized as suggested by van der Burgt *et al.*⁷⁷ The three sets of cross sections are consistent with each other within the combined uncertainties ($\pm 30\%$ for Aarts and de Heer,⁸⁵ $\pm 22\%$ for Mumma and Zipf⁸⁷ and $\pm 22\%$ for Ajello and Shemansky⁵⁸).

(4) $N^+\ 2p\ ^3D^\circ-2p\ ^3P$ at 108.4 nm. Two sets of cross sections (by Aarts and de Heer⁸⁵ and James *et al.*⁶⁸) are compared in Fig. 21. Although their maximum positions are

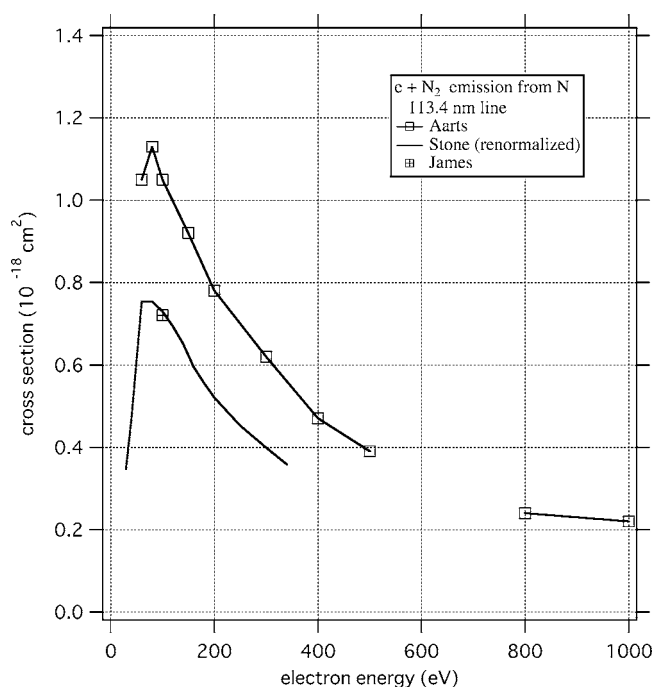


FIG. 17. Cross sections for the emission of 113.4 nm line of N. Three sets of measured values are compared: Aarts and de Heer,⁸⁵ Stone and Zipf⁸⁶ (renormalized), and James *et al.*⁶⁸

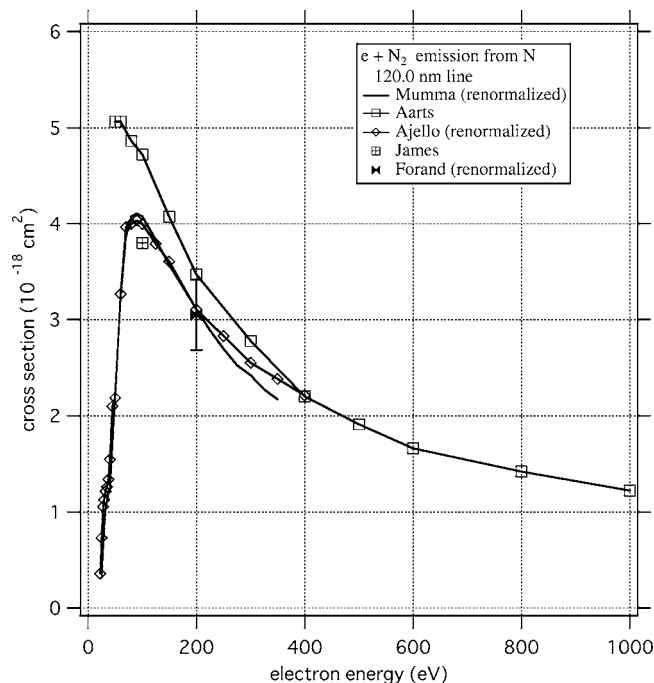


FIG. 18. Cross sections for the emission of 120.0 nm line of N. Five sets of measured values are compared: Mumma and Zipf⁸⁷ (renormalized), Aarts and de Heer,⁸⁵ Ajello and Shemansky⁵⁸ (renormalized), James *et al.*,⁶⁸ and Forand *et al.*⁸⁸ (renormalized).

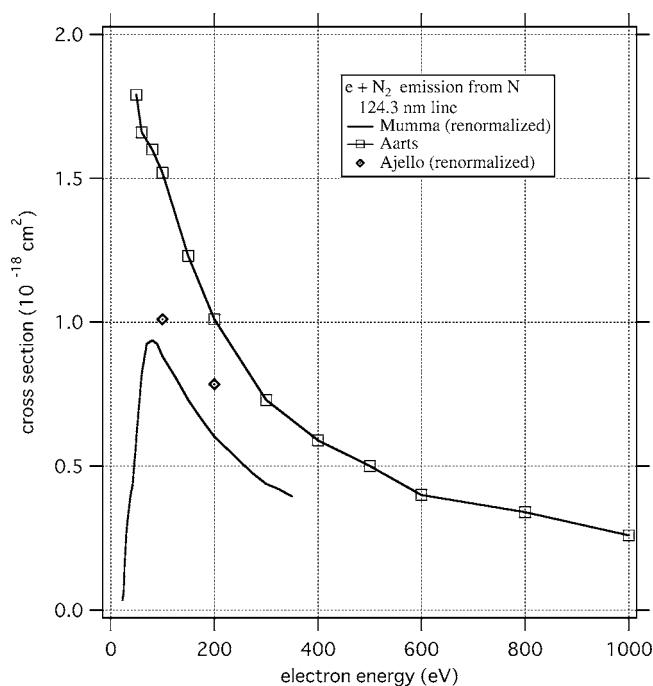


FIG. 19. Cross sections for the emission of 124.3 nm line of N. Three sets of measured values are compared: Mumma and Zipf⁸⁷ (renormalized), Aarts and de Heer,⁸⁵ and Ajello and Shemansky⁵⁸ (renormalized).

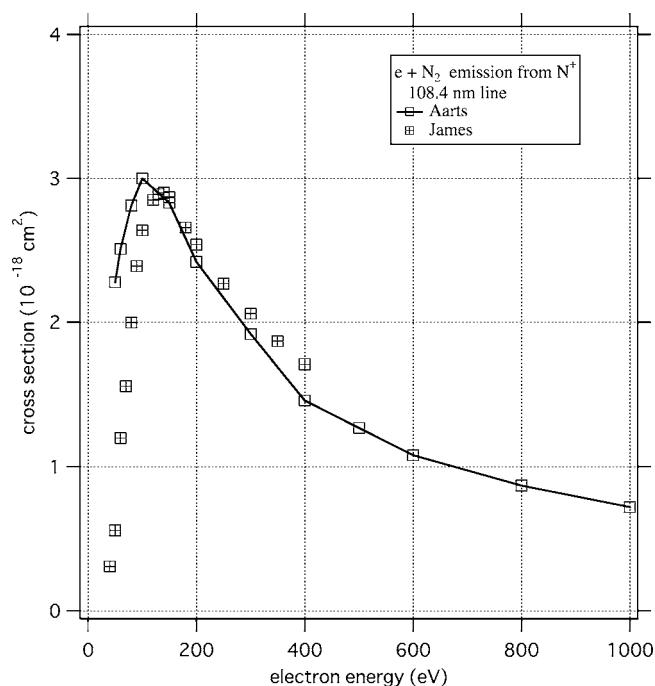


FIG. 21. Cross sections for the emission of 108.4 nm line of N^+ . Two sets of measured values are compared: Aarts and de Heer⁸⁵ and James *et al.*⁶⁸

slightly different from one another, the two sets of values are consistent with each other.

8. Total Dissociation Cross Section for Neutral Products

Winters⁸⁹ determined the total dissociation cross section for neutral products Q_{diss} by the measurement of a change of pressure in a gas cell. When a dissociation occurs, the pressure decreases due to the adsorption of the dissociation fragment to the wall of the cell. In 186, it was suggested that the Q_{diss} of Winters was too large and may include a contribution of dissociative ionization.

Cosby⁹⁰ obtained Q_{diss} by directly detecting the fragment pair, $N+N$. The corresponding dissociation energy is 9.7537 eV. With the use of a fast N_2 beam, the correlated pair $N+N$ was detected by a time and position sensitive detector. Cosby compared his cross section with Winters' values corrected for dissociative ionization. Cosby's values were systematically larger than the Winters' values, but those two sets were consistent with each other within the combined uncertainties ($\pm 30\%$ for Cosby and $\pm 20\%$ for Winters). Then Cosby suggested that the best values are a weighted average of these two sets of cross sections. Those suggested cross sections are shown in Fig. 22 and Table 14.

Mi and Bonham⁹¹ obtained a wide range of energy loss spectrum in a pulsed electron beam TOF experiment. From the spectrum, they derived an elastic cross section and a total inelastic cross section. The sum of the two cross sections was normalized to the total scattering cross section measured by Kennerly¹¹ to determine the absolute scale of the former. In a

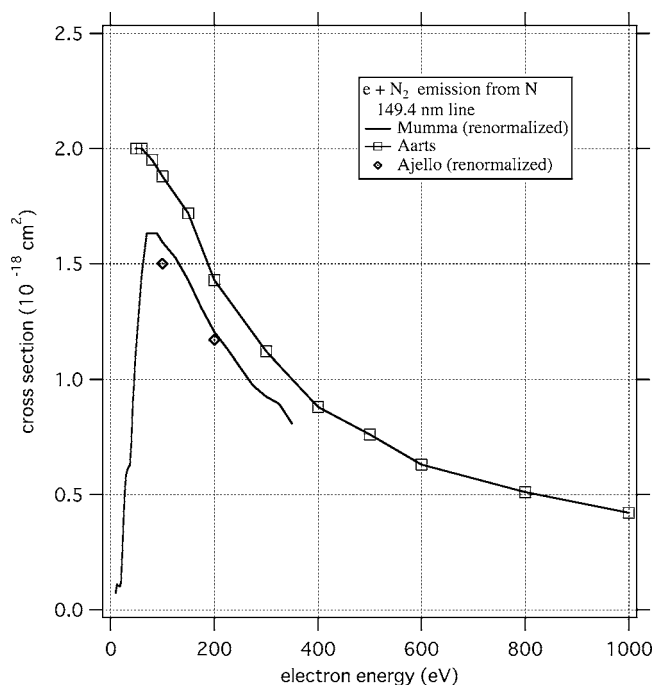


FIG. 20. Cross sections for the emission of 149.4 nm line of N. Three sets of measured values are compared: Mumma and Zipf⁸⁷ (renormalized), Aarts and de Heer,⁸⁵ and Ajello and Shemansky⁵⁸ (renormalized).

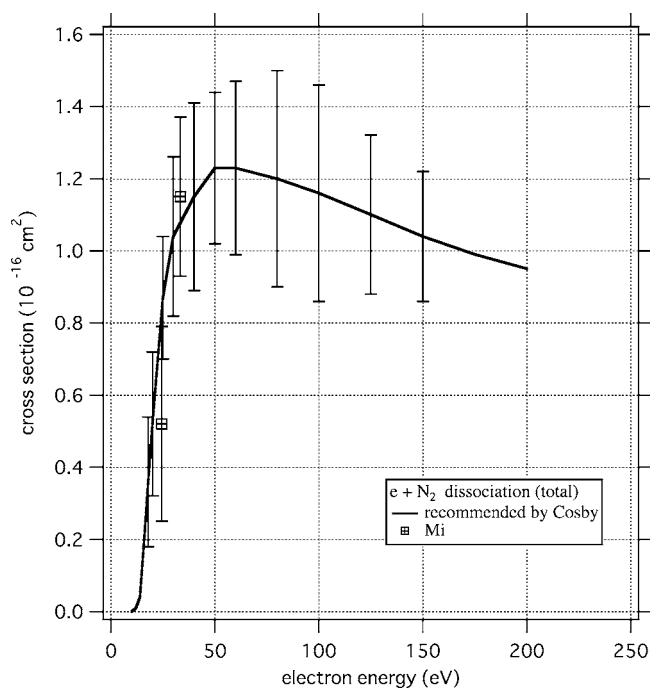


FIG. 22. Total dissociation cross section of N_2 . Recommended values of Cosby⁹⁰ are compared with the measured ones of Mi and Bonham.⁹¹

similar manner, but in coincidence with ion detection, they obtained the total ionization cross section. Subtracting the total ionization cross section from the total inelastic one, they obtained the “excitation+dissociation” cross section. Then they estimated the total “excitation” cross section with the data summarized in I86. Finally the total “dissociation” cross section, Q_{diss} , was derived by subtracting the total “excitation” cross section from the “excitation + dissociation” cross section. They have done the experiment at three points of electron energy: 24.5, 33.1, and 33.6 eV. At the final stage, they took an average of the values at

TABLE 14. Total dissociation cross section for electron collisions with N_2 recommended by Cosby⁹⁰

| Energy (eV) | Cross section (10^{-16} cm^2) |
|-------------|---|
| 10 | 0 |
| 12 | 0.01 |
| 14 | 0.04 |
| 16 | 0.20 |
| 18 | 0.36 |
| 20 | 0.52 |
| 25 | 0.87 |
| 30 | 1.04 |
| 40 | 1.15 |
| 50 | 1.23 |
| 60 | 1.23 |
| 80 | 1.20 |
| 100 | 1.16 |
| 125 | 1.10 |
| 150 | 1.04 |
| 175 | 0.99 |
| 200 | 0.95 |

TABLE 15. Recommended ionization cross sections for $e + N_2$ (Part 1)

| Energy (eV) | N_2^+ (10^{-16} cm^2) | N^+ (10^{-16} cm^2) | N^{++} (10^{-16} cm^2) | Total (10^{-16} cm^2) |
|-------------|-------------------------------------|-----------------------------------|--------------------------------------|-----------------------------------|
| 16 | 0.0211 | | | 0.0211 |
| 16.5 | 0.0466 | | | 0.0466 |
| 17 | 0.0713 | | | 0.0713 |
| 17.5 | 0.0985 | | | 0.0985 |
| 18 | 0.129 | | | 0.129 |
| 18.5 | 0.164 | | | 0.164 |
| 19 | 0.199 | | | 0.199 |
| 19.5 | 0.230 | | | 0.230 |
| 20 | 0.270 | | | 0.270 |
| 20.5 | 0.308 | | | 0.308 |
| 21 | 0.344 | | | 0.344 |
| 21.5 | 0.380 | | | 0.380 |
| 22 | 0.418 | | | 0.418 |
| 22.5 | 0.455 | | | 0.455 |
| 23 | 0.492 | | | 0.492 |
| 23.5 | 0.528 | | | 0.528 |
| 24 | 0.565 | | | 0.565 |
| 24.5 | 0.603 | | | 0.603 |
| 25 | 0.640 | | | 0.640 |
| 30 | 0.929 | 0.0325 | | 0.962 |
| 35 | 1.16 | 0.0904 | | 1.25 |
| 40 | 1.37 | 0.166 | | 1.54 |

the latter two points and reported Q_{diss} at 24.5 and 33.4 eV. Their results are compared in Fig. 22 with the values recommended by Cosby. A good agreement is seen between the two sets of data.

9. Ionization

9.1. Partial and Total Ionization Cross Sections

After reviewing all the available experimental data, Lindsay and Mangan⁹² have determined the recommended values of partial and total ionization cross sections for N_2 . They put much stress on the reliability of the experimental methods employed. In particular, methods capable of collecting all the product ions are preferred and a greater weight is placed on the experiment not relying on normalization to other works. As a result, their recommended values are based on the measurement by Straub *et al.*,⁹³ who used a TOF mass spectrometer to detect product ions. It should be noted that Straub *et al.* made their cross sections absolute independently, i.e., without resorting to any other data for normalization. In the energy region below 25 eV, the cross section for the production of N_2^+ completely agrees with the total ionization cross section measured by Rapp and Englander-Golden.⁹⁴ In that energy region, no significant production of other ions takes place. (The appearance potential of N^+ is 24.34 eV, while the best value of the ionization energy of N_2 is 15.581 eV.) Since the measurement by Straub *et al.* has fewer data points in the region, Lindsay and Mangan adopted the total ionization cross section of Rapp and Englander-Golden as the recommended values for the production of N_2^+ below 25 eV. Tables

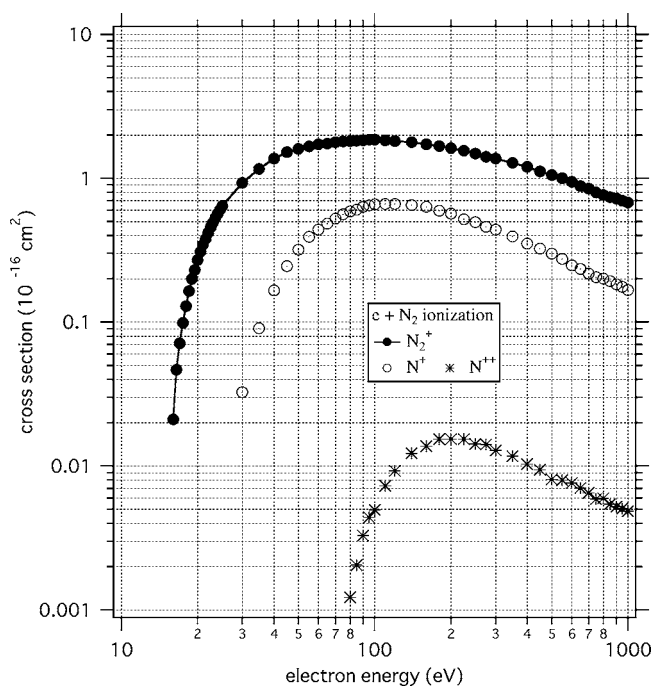
TABLE 16. Recommended ionization cross sections for $e + N_2$ (Part 2)

| Energy (eV) | N_2^+ (10^{-16} cm^2) | N^+ (10^{-16} cm^2) | N^{++} (10^{-16} cm^2) | Total (10^{-16} cm^2) |
|----------------|--|--------------------------------------|---|--------------------------------------|
| 45 | 1.52 | 0.245 | | 1.77 |
| 50 | 1.60 | 0.319 | | 1.91 |
| 55 | 1.66 | 0.390 | | 2.05 |
| 60 | 1.72 | 0.438 | | 2.16 |
| 65 | 1.74 | 0.482 | | 2.22 |
| 70 | 1.78 | 0.523 | 0.000171 | 2.30 |
| 75 | 1.80 | 0.561 | 0.000658 | 2.36 |
| 80 | 1.81 | 0.587 | 0.00122 | 2.40 |
| 85 | 1.82 | 0.605 | 0.00204 | 2.43 |
| 90 | 1.83 | 0.632 | 0.00328 | 2.47 |
| 95 | 1.85 | 0.645 | 0.00439 | 2.50 |
| 100 | 1.85 | 0.656 | 0.00495 | 2.51 |
| 110 | 1.83 | 0.660 | 0.00725 | 2.50 |
| 120 | 1.81 | 0.661 | 0.00927 | 2.48 |
| 140 | 1.78 | 0.652 | 0.0122 | 2.45 |
| 160 | 1.72 | 0.633 | 0.0137 | 2.36 |
| 180 | 1.67 | 0.595 | 0.0154 | 2.28 |
| 200 | 1.61 | 0.566 | 0.0154 | 2.19 |
| 225 | 1.55 | 0.516 | 0.0154 | 2.08 |
| 250 | 1.48 | 0.493 | 0.0142 | 1.98 |
| 275 | 1.41 | 0.458 | 0.0141 | 1.89 |
| 300 | 1.37 | 0.438 | 0.0128 | 1.82 |

15, 16, 17, and Fig. 23 give the cross sections for the production of N_2^+ , N^+ , and N^{++} as recommended by Lindsay and Mangan. (It should be noted that they slightly changed the original values reported by Straub *et al.*, due to a recent recalibration of their apparatus.) An absolute uncertainty of the recommended cross section was estimated to be $\pm 5\%$ for N_2^+ and N^+ and $\pm 6\%$ for N^{++} . The cross section for N^+ may include a contribution of N_2^{++} , because the mass spectrometer used cannot discriminate the ions having the same charge-to-mass ratio. Following the suggestion by Tian and Vidal,⁹⁵ the contribution is estimated from the cross section for CO (isoelectronic to N_2). According to the review by Lindsay and Mangan,⁹² the cross sections for the production of CO^+ and CO^{++} are 1.94×10^{-16} and $8.21 \times 10^{-19} \text{ cm}^2$ at 100 eV (near the peak of the cross section curve). Thus the

TABLE 17. Recommended ionization cross sections for $e + N_2$ (Part 3)

| Energy (eV) | N_2^+ (10^{-16} cm^2) | N^+ (10^{-16} cm^2) | N^{++} (10^{-16} cm^2) | Total (10^{-16} cm^2) |
|----------------|--|--------------------------------------|---|--------------------------------------|
| 350 | 1.28 | 0.393 | 0.0117 | 1.68 |
| 400 | 1.20 | 0.351 | 0.0103 | 1.56 |
| 450 | 1.11 | 0.324 | 0.00940 | 1.45 |
| 500 | 1.05 | 0.299 | 0.00808 | 1.36 |
| 550 | 0.998 | 0.274 | 0.00796 | 1.28 |
| 600 | 0.943 | 0.248 | 0.00760 | 1.20 |
| 650 | 0.880 | 0.234 | 0.00701 | 1.12 |
| 700 | 0.844 | 0.217 | 0.00649 | 1.07 |
| 750 | 0.796 | 0.205 | 0.00587 | 1.01 |
| 800 | 0.765 | 0.200 | 0.00594 | 0.971 |
| 850 | 0.738 | 0.192 | 0.00543 | 0.936 |
| 900 | 0.719 | 0.183 | 0.00522 | 0.907 |
| 950 | 0.698 | 0.176 | 0.00505 | 0.879 |
| 1000 | 0.676 | 0.167 | 0.00485 | 0.847 |

FIG. 23. Recommended values of ionization cross section of N_2 for the productions of N_2^+ , N^+ , and N^{++} .

ratio of the doubly to singly charged ions of the parent molecule produced is less than 0.5%. If this can be also applied to N_2 , the contribution of N_2^{++} can be ignored within the error limit of the cross section of N^+ .

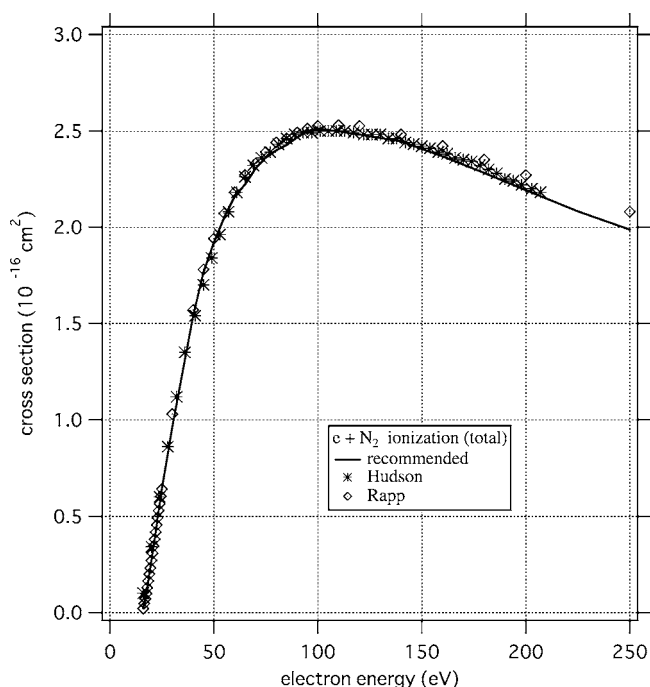
FIG. 24. Total ionization cross sections of N_2 . The recommended values are compared with the results of total ion current measurement by Rapp and Englander-Golden⁹⁴ and Hudson *et al.*⁹⁶

TABLE 18. Cross sections (in 10^{-17} cm^2) for the electron impact ionization excitation of N_2 at 100 eV

| State of N_2^+ | Doering ⁹⁹ | Van Zyl ¹⁰⁰ | Present estimate |
|-------------------------|--------------------------|------------------------|------------------|
| $X \ ^2\Sigma_g^+$ | 8.69 (0.70) ^a | 6.05 (2.7) | 7.03 |
| $A \ ^2\Pi_u$ | 8.79 (0.70) | 10.11 (1.9) | 8.71 |
| $B \ ^2\Sigma_u^+$ | 1.92 (0.33) | 2.74 (0.27) | 2.36 |

^aPossible errors estimated.

The total ionization cross section has been obtained as the sum of all the partial cross sections and also given in Tables 15–17. Lindsay and Mangan estimated an absolute uncertainty of $\pm 5\%$ for them. The resulting total cross section is compared in Fig. 24 with the values of Rapp and Englander-Golden.⁹⁴ The two sets of the cross sections are in good agreement within the combined error limits ($\pm 5\%$ for Lindsay and Mangan and $\pm 7\%$ for Rapp and Englander-Golden), although the values of Rapp and Englander-Golden are systematically larger than those recommended here above 200 eV. Rapp and Englander-Golden obtained their cross sections with the use of total ion current measurement. Recently Hudson *et al.*⁹⁶ measured the total ionization cross section also using the total ion current measurement technique. As is shown in Fig. 24, their values (with $\pm 5\%$ accuracy) completely agree with the present recommended data. They made their measurement up to 200 eV.

Tian and Vidal⁹⁵ also measured the partial ionization cross sections for N_2 . Their values, though with a rather large uncertainty ($\pm 10\%$), are consistent with the present data. They also determined the branching ratio of each dissociation channel. For example, they obtained the cross sections for the production of N^+ separately for the channels, $\text{N}^+ + \text{N}$, $\text{N}^+ + \text{N}^+$, and $\text{N}^+ + \text{N}^{++}$.

9.2. Excited States of N_2^+

An electron impact on N_2 produces the molecular ion N_2^+ , not only in its ground state but also in its excited one. Doering and his colleagues developed an electron–electron coincidence technique [the so called ($e,2e$) method] to detect the scattered incident electron and the emitted secondary electron in coincidence. From the energy analysis of the electrons involved, the electronic state of the product ion can be determined unambiguously. After two preliminary attempts,^{97,98} they⁹⁹ finally obtained the cross sections for the production of N_2^+ ($X \ ^2\Sigma_g^+$, $A \ ^2\Pi_u$, $B \ ^2\Sigma_u^+$) as shown in Table 18. The A and B states are located at 1.118 and 3.170 eV above the ground (X) state of N_2^+ , respectively (see Table 7).

N_2^+ in the A and B states emit radiation. From the emission cross section, we can derive the corresponding excitation cross section (see Sec. 7). Van Zyl and Pendleton¹⁰⁰ took that way to derive excitation cross section. After reviewing previous experiments, they determined the best value of the Q_{emis} for the (0,0) band (at 391.4 nm) of the first negative system (the $B-X$ transition of N_2^+) to be $1.72 \times 10^{-17} \text{ cm}^2$ at 100 eV. From the emission measurements of the Meinel (the

$A-X$ transition of N_2^+) and the first negative systems, they obtained the ratio $Q_{\text{exc}}[\text{N}_2^+(A)]/Q_{\text{exc}}[\text{N}_2^+(B)]$ to be 3.69 at 100 eV. Then they took the ionization cross section $Q_{\text{ion}}(\text{N}_2^+) = 18.9 \times 10^{-17} \text{ cm}^2$ at 100 eV from the measurement by Straub *et al.*⁹³ (They took into account 2% correction for the production of N_2^+ in states other than X , A , and B .) Finally they determined the cross sections for the productions of X , A , and B states of N_2^+ as shown in Table 18.

There is a significant discrepancy between the two sets of cross sections of Doering and Yang⁹⁹ and Van Zyl and Pendleton.¹⁰⁰ Generally it is difficult to determine ionization cross section with the ($e,2e$) method. In principle, electrons should be detected all over the scattering and ejection angles. Here a compromise of the ($e,2e$) and the emission methods is taken to obtain the relevant cross sections. This was originally suggested by Doering and Yang.⁹⁹ From the results of their own ($e,2e$) measurement and previous optical experiments together, Doering and Yang⁷³ determined the best value of the Q_{emis} for the (0,0) band at 391.4 nm of the first negative system to be $1.48 \times 10^{-17} \text{ cm}^2$ at 100 eV. From this value, $Q_{\text{exc}}[\text{N}_2^+(B)]$ is estimated to be $2.36 \times 10^{-17} \text{ cm}^2$ at 100 eV. With the use of the same ratio $Q_{\text{exc}}[\text{N}_2^+(A)]/Q_{\text{exc}}[\text{N}_2^+(B)]$ as adopted by Van Zyl and Pendleton, we obtain $Q_{\text{exc}}[\text{N}_2^+(A)] = 8.71 \times 10^{-17} \text{ cm}^2$ at 100 eV. Then, using the value of $Q_{\text{ion}}(\text{N}_2^+)$ recommended in the present paper (Table 16), we finally have the cross sections shown in Table 18. As is described below, Abramzon *et al.*¹⁰¹ measured the cross section for the production of $\text{N}_2^+(X)$ at electron energies from 15 to 180 eV. Their cross section at 100 eV [i.e., $(7.49 \pm 0.75) \times 10^{-17} \text{ cm}^2$] is closer to the present estimate than to the value of Doering and Yang, or Van Zyl and Pendleton.

Abramzon *et al.*¹⁰¹ determined the $Q_{\text{exc}}[\text{N}_2^+(X)]$ with the laser induced fluorescence technique. They observed the laser induced emission of the $B \ ^2\Sigma_u^+ \rightarrow X \ ^2\Sigma_g^+$ transition of N_2^+ at 391 nm. They normalized their data by comparing this to the laser induced emission of the $3 \ ^3P \rightarrow 2 \ ^3S$ transition of He and using the absolute value of the cross section for the electron-impact excitation of the $2 \ ^3S$ state of He. The resulting values are shown in Fig. 25. For comparison, the figure also shows the present recommended values of the partial ionization cross section for the production of N_2^+ (shown in Fig. 23). Abramzon *et al.* claimed $\pm 10\%$ error for their result. Their cross sections near threshold seem to have larger uncertainty. This would be caused by the weak intensity of the fluorescence due to the small probability of ionization near threshold.

Doering and Yang⁹⁹ discussed the energy dependence of the branching ratios, $Q_{\text{exc}}[\text{N}_2^+(X,A,B)]/Q_{\text{ion}}(\text{total})$. According to their conclusion, the ratio $Q_{\text{exc}}[\text{N}_2^+(B)]/Q_{\text{ion}}(\text{total})$ does not change above 100 eV (within $\pm 10\%$). The ratio $Q_{\text{exc}}[\text{N}_2^+(A)]/Q_{\text{ion}}(\text{total})$ is also almost constant (within $\pm 20\%$) above 50 eV.

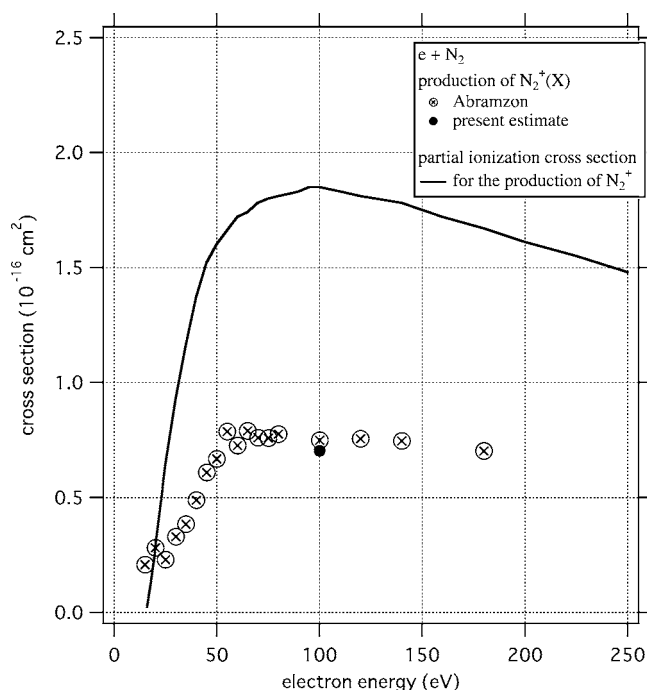


FIG. 25. Cross sections for the production of $N_2^+(X)$. The measured values of Abramzon *et al.*¹⁰¹ are compared with the present estimate given in Table 18. For comparison, the partial ionization cross sections for the N_2^+ production are reproduced from Fig. 23.

9.3. Emission from N_2^{+*}

Since the publication of I86, no measurement of Q_{emis} has been reported for the radiation from N_2^{+*} . In I86, the cross

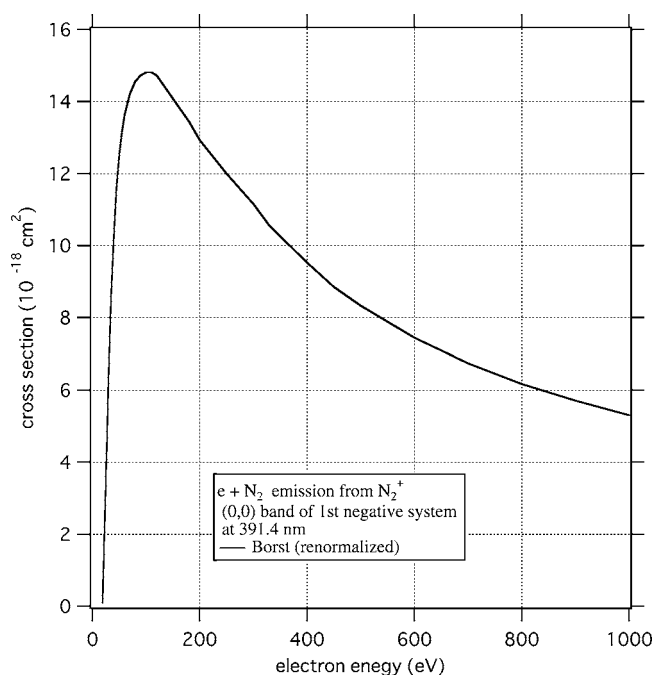


FIG. 26. Cross sections for the emission of the (0,0) band (at 391.4 nm) of the first negative system of N_2^+ . The measured values of Borst and Zipf⁷² are plotted after renormalization (see text).

TABLE 19. Cross sections for the emission of the (0,0) band of first negative system (at 391.4 nm) for the electron collision with N_2

| Energy (eV) | Cross section (10^{-18} cm^2) | Energy (eV) | Cross section (10^{-18} cm^2) |
|-------------|---|-------------|---|
| 19 | 0.103 | 100 | 14.8 |
| 19.2 | 0.205 | 110 | 14.8 |
| 19.6 | 0.408 | 120 | 14.7 |
| 20 | 0.608 | 140 | 14.3 |
| 21 | 1.15 | 160 | 13.9 |
| 22 | 1.68 | 180 | 13.4 |
| 23 | 2.22 | 200 | 12.9 |
| 24 | 2.77 | 250 | 12.0 |
| 25 | 3.31 | 300 | 11.1 |
| 26 | 3.86 | 330 | 10.6 |
| 27 | 4.41 | 400 | 9.53 |
| 30 | 6.10 | 450 | 8.85 |
| 35 | 8.60 | 500 | 8.33 |
| 40 | 10.3 | 600 | 7.45 |
| 45 | 11.6 | 700 | 6.74 |
| 50 | 12.5 | 800 | 6.17 |
| 55 | 13.1 | 900 | 5.70 |
| 60 | 13.6 | 1000 | 5.30 |
| 70 | 14.2 | | |
| 80 | 14.6 | | |
| 90 | 14.7 | | |

section measured by Borst and Zipf⁷² was cited as a representative value of the Q_{emis} for the (0,0) band of the first negative system at 391.4 nm. If the values are renormalized to the best values determined by Doering and Yang⁷³ at 100 eV, the former cross sections should be multiplied by 0.871. The renormalized cross sections are shown in Fig. 26 and Table 19.

9.4. Differential Cross Sections

Energy distribution of the secondary electrons ejected upon ionizing collisions are necessary when the energy deposition of the incident electron is evaluated. There are several measurements of the angular and energy distribution [the so-called doubly differential cross section (DDCS) for ionization] of the secondary electrons from N_2 . From these measurements, the energy distribution [the singly differential cross section, (SDCS) for ionization] has been derived. In I86, the result of Opal *et al.*¹⁰² was cited. Later Goruganthu *et al.*¹⁰³ made a measurement of DDCS at 200, 500, 1000, and 2000 eV of the incident electron energy. Figure 27 compares the SDCS of Goruganthu *et al.* with those given in I86 (based on Opal *et al.*). A small difference is seen at the lowest energies of the secondary electron, but an overall agreement is good between the two sets of data. Thus the SDCS presented in I86 can be used for application, with a special caution at the lowest energies of the secondary electrons.

10. Summary and Future Problems

Cross sections for electron collisions with nitrogen molecules are summarized in Fig. 28. They are as follows:

- total scattering cross section, Q_T (Table 2);

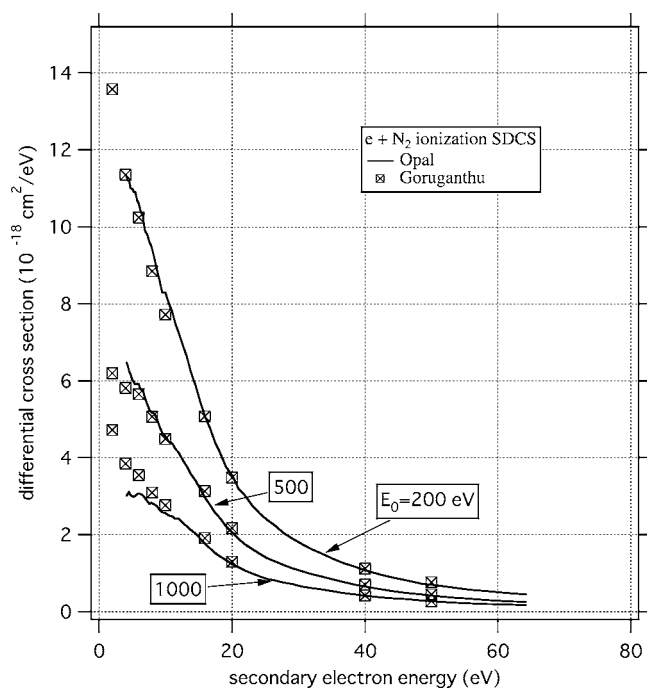


FIG. 27. Energy distributions of the secondary electrons emitted upon electron-impact ionization of N_2 . The values of Opal *et al.*¹⁰² are compared with the measurement of Goruganthu *et al.*¹⁰³ The energy of the incident electron E_0 is indicated.

- (ii) elastic scattering cross section, Q_{elas} (Table 3);
- (iii) momentum-transfer cross section, Q_m (Table 4);
- (iv) rotational cross section for the transition $J=0 \rightarrow 2$, $Q_{\text{rot}} (J=0 \rightarrow 2)$ (Table 5);
- (v) vibrational cross section for the transition $v=0 \rightarrow 1$, $Q_{\text{vib}} (v=0 \rightarrow 1)$ (Table 6 and Fig. 7);
- (vi) a few representative cross sections for the excitation of electronic states (Tables 8, 9, 10);
- (vii) total dissociation cross section, Q_{diss} (Table 14); and

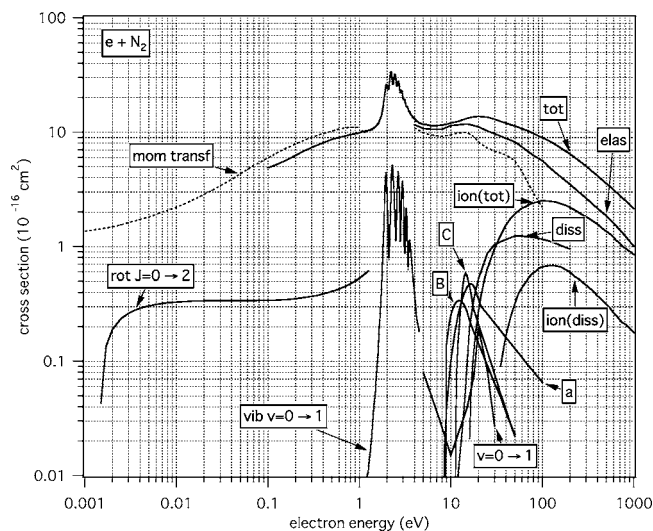


FIG. 28. Summary of the electron collision cross sections for N_2 .

- (viii) total, $Q_{\text{ion}}(\text{total})$, and dissociative, $Q_{\text{ion}}(\text{diss})$, ionization cross sections (Tables 15, 16, 17). Here $Q_{\text{ion}}(\text{diss})$ is defined as $Q_{\text{ion}}(N^+) + 2Q_{\text{ion}}(N^{++})$.

To be consistent with each other, those cross sections should follow the relation

$$Q_T = Q_{\text{elas}} + Q_{\text{ion}}(\text{total}) + Q_{\text{diss}} + \sum Q_{\text{exc}}. \quad (8)$$

The last term on the right side of the equation includes all the excitation cross sections of discrete (rotational, vibrational, electronic) states. It should be noted that the excitation of those states which are known to predissociate must be excluded in the summation. As far as the cross sections shown in Fig. 28 are concerned, the above relation holds within the combined uncertainties claimed for the cross sections.

As is stated in Sec. 1, the present paper serves as a complete update of the data compilation for the $e + N_2$ collisions, previously reported by the present author and his colleagues (i.e., I86). As far as any new information is available, the previous data reported in I86 have been re-evaluated to update the conclusion. Actually all the previous conclusions have been revised, except for excitation of a few high-lying electronic states. As is shown in each section, however, further studies are still needed to make the cross section data more comprehensive and more accurate. In particular, the following problems should be addressed:

- (1) Some controversy exists among the values of Q_T measured at the energies below 1 eV. Considering its unique importance (i.e., giving an upper limit of any cross section), the absolute value of Q_T should be determined as accurately as possible.
- (2) Experimental cross sections (ICS) above 0.2 eV are lacking for rotational transitions. Theory indicates that the values are expected to be large.
- (3) Much more refinement is needed for the measurement of the excitation cross section for electronic states. Most of the recommended data for the processes have a large uncertainty. This reflects a significant difference in the DCS measured by different groups. Furthermore, the cross section for the excitation of higher states (i.e., those with threshold above 12.5 eV) is still very uncertain. Those higher states include a dipole-allowed one, which may have a large cross section even at a high energy of electrons. Furthermore many of them are known to predissociate.
- (4) The total dissociation cross sections are now available with fair certainty. Further information is necessary for the details of the dissociation products. How much fraction of the nitrogen atoms are produced in their ground state? Also important is the cross section for the production of nitrogen atoms in their metastable states: 2P or 2D .
- (5) Finally, cross sections dealt with in the present paper can depend on the internal state of the target molecule. The experimental data shown in the preceding sections, however, have been collected from the measurements at

room temperature. Any study of the dependence of the cross section on the gas temperature may be useful for practical applications, although fragmentary information is available for that (see a review by Christophorou and Olthoff¹⁰⁴).

11. Acknowledgments

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